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CHARACTERIZATION OF GRAPHITE LITHIUM-ION CELLS

by

Steven D. Moseley

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Thesis Advisor: James A. Horning Second Reader: Ronald L. Phelps

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CHARACTERIZATION OF GRAPHITE LITHIUM-ION CELLS

Steven D. Moseley Major, United States Army B.S., Rocky Mountain College, 1994

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Author: Steven D. Moseley

Approved by: James A. Horning

Thesis Advisor

Ronald L. Phelps Second Reader

Rudolf Panholzer

Chairman, Space Systems Academic Group

ABSTRACT

This thesis explores the characterization of graphite lithium-ion cells. A control procedure was performed to ensure any capacity loss or gain seen in tests was not the result of cell cycling. Vibration testing of the cells, on all three axes to simulate the spacecraft launch environment, showed a slight increase in capacity after vibration. Cell capacity was measured at two current rates at a variety of temperatures to obtain a family of curves to allow for a prediction of cell capacity at a given temperature. Voltage drift was explored and determined to not be a factor when matching cells for a battery. Using data from hard carbon lithium-ion cells, data for capacity loss over time, while in storage, was examined. It was determined that for an 18-month time period, these cells lost less than 2% of their capacity while in storage. Next, cells were cycled in simulated Low Earth Orbit power cycling to determine capacity loss while on orbit. Using a 0.25 Amp charge rate, the graphite cells retained 93% of their initial starting capacity by the 2,000th cycle. Finally, cells underwent accelerated Low Earth Orbit testing to validate the accelerated testing theory. This thesis concludes that accelerated testing is not a good representation of how cells will perform under real-time conditions.

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EXECUTIVE SUMMARY

When it comes to satellites, the space industry is looking to put more payload on a spacecraft and reduce costs. One way to accomplish this is to reduce the weight of spacecraft components. However, the increasing need for more power for the payload requires more battery capacity. The answer to this problem is lithium-ion batteries. Lithium-ion batteries, with their high energy density, can provide a means for reducing spacecraft weight and thus provide more payload capacity.

In this thesis, the characteristics of graphite lithium-ion cells are explored and analyzed. As compared to coke and hard carbon cells, graphite cells have a flatter discharge curve, resulting in a more constant voltage throughout the discharge cycle. Because of this characteristic, graphite cells appear to be a better solution. The characteristics of graphite cells are explored and analyzed. Additionally, Low Earth Orbit testing was performed to determine how the cells will react on orbit. Finally, accelerated Low Earth Orbit testing was performed to determine if it was a valid way to speed up the testing process of graphite lithium-ion cells.

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I. INTRODUCTION

A. BACKGROUND OF LITHIUM-ION TECHNOLOGY

As the lightest metallic element, lithium generates a high voltage as compared to the highest Standard Hydrogen Electrode. This combination makes employing lithium metal as the active ingredient in a rechargeable cell a very desirable option. In early lithium-ion development, lithium metal was used in combination with a transition metal oxide or sulphide intercalation compound. This is a compound that allows lithium ions to attach and detach multiple times without altering the compound.[1] However, these attempts resulted in a limited cycle life and a poor safety record.[2]

As development continued, a carbon material was used on the anode instead of the lithium metal. Carbon was selected as it can reversibly intercalate Li⁺. At the present time, there are three types of carbon used in the anode of lithium-ion cells. These three types are hard carbon, graphite, and coke.[2] Of the three types of anodes, graphite offers the flattest discharge curve over coke and hard carbon.[3], [4]

B. REASONS FOR RESEARCH

This thesis examines the characteristics of graphite lithium-ion cells. Before designing a battery comprised of graphite lithium-ion cells, it is important to understand all cell characteristics. Cell characteristics include, but are not limited to, effects of the spacecraft launch environment, cell performance over a specified temperature range, cell capacity versus time, self discharge, and cell capacity versus charge cycles. Having an in-depth understanding of the cells will allow one to determine the proper way to build a battery comprised of these cells.

C. RESEARCH OVERVIEW

The characteristics of graphite lithium-ion were obtained through performing multiple tests on the cells. To the greatest extent possible, cells undergoing testing were

brand new cells which had never been cycled except for the initial charge they received when manufactured. Additionally, three cells underwent the same procedure at the same rate for each test.

The first test was a control procedure, which was used to identify capacity loss related to cell cycling so it could be accounted for in other procedures. This test performed twenty full charge/discharge cycles on individual cells and measured the capacity loss after each cycle.

The second test was a random vibration test which was used to determine the effects, if any, that vibrations similar to those experienced during a spacecraft launch will have on cell capacity. Each cell underwent random vibrations on each of its three axes, with a capacity measurement being performed after each axis random vibration.

The third test measured the cell's discharge capacity at two separate current rates over a range of temperatures. This produced a family of curves which will allow for a prediction of the expected discharge cell capacity at a given temperature. The temperatures for this test varied from a low temperature of 5° C to a high temperature of 40° C in 5° C increments.

The fourth test measured voltage drift after completion of a charge or discharge cycle. At the completion of a charge or discharge cycle, the cell voltage will increase or decrease slightly depending on the final state of charge. This test is used to determine if voltage drift needs to be considered when matching individual graphite cells for a battery.

The fifth test measured capacity loss in storage for hard carbon lithium-ion cells. There is not enough test data from the graphite cells at the Naval Postgraduate School to determine capacity loss in storage. However, there is sufficient data from hard carbon cells to get a general idea. While this data cannot be directly correlated to graphite cells, it can be used as a reference to explore this phenomenon.

The sixth test simulated the cycling of a battery during low earth orbit. It consists of sixty minutes of charging, followed by 30 minutes of discharging. This correlates to a low earth orbit satellite, which is in sunlight approximately sixty minutes, followed

by eclipse for 30 minutes. Capacity measurements are being performed every 200th cycle to determine how much capacity the battery will lose over time and how long the battery will last.

The seventh and final test is a validation of accelerated testing of the cycling of a battery during low earth orbit. It consists of 30 minutes of charging, followed by fifteen minutes of discharging. Although in these tests, the charge and discharge rates will be twice what they were in the previous test. This amounts to the same energy in and out of the cell during an orbit. The theory goes that since it is the same energy in and out, one can determine how the cell will perform in half the time. This procedure will test the validity of the theory and determine whether it is an accurate representation of long term testing.

Based on the results of the above listed tests, there will be some conclusions and recommendations for future testing.

II. SONY US18650 GRAPHITE LITHIUM-ION CELLS

A. PHYSICAL DESCRIPTION

Sony US18650 graphite lithium-ion cells are cylindrical cells 18 mm in diameter and 65 mm in length, and have a mass of approximately 45 grams. The cells are comprised of multiple layers of anode and cathode material. The anode is graphite, while the cathode is Lithium Cobalt Di-oxide (LiCoO₂).[5] In between the anode and cathode is a plastic separator material. These layers are then encased with electrolyte in the cylindrical can. The physical outside of the can is the negative anode. The positive cathode is a top cover slightly smaller than the diameter of the cell and separated from the outside of the can by an insulator. There are safety vents built in directly below the positive terminal to allow for venting to ensure the cell does not explode during a catastrophic failure. The outside of the cell is covered with an insulated cover, with only the bottom of the cell open for electrical connection.

B. HOW A GRAPHITE LITHIUM-ION CELL WORKS

The power both in and out of the cell is produced through the migration of lithium ions between the anode and cathode through a lithium conducting electrolyte. This migration results in electron exchange, which is the electrical current, through the anode and cathode. More specifically, during charging, lithium ions are removed from the cathode, a process called undoping. These lithium ions are then inserted onto the anode, a process called doping. As the charging moves electrons from the cathode to the anode, it produces a negative charge in the anode, which causes the positively charged lithium ions to travel to the anode, resulting in the doping of the anode. For discharging, the process is reversed, where the cathode is doped, and the anode is undoped. This chemical reaction is depicted in Figure 1. [2]

Discharging -->

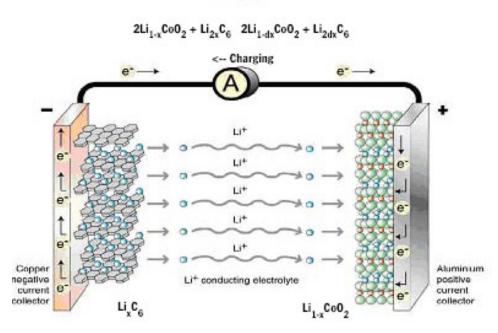


Figure 1. Chemical reaction of a lithium-ion cell (From: [2]).

When the cell is manufactured, it has no capacity. A chemical reaction occurs during the initial charging in which lithium ions migrate from the lithium compound of the cathode to the carbon material of the anode. The chemical reaction for this initial charge is $\text{LiCoO}_2 \rightarrow \text{Li}_{1-x}\text{CoO}_2 + \text{Li}_x\text{C}$. This is the initial transportation of the lithium ions from the cathode to the anode. After the initial charge, the chemical reaction is $\text{Li}_{1-x}\text{CoO}_2 + \text{Li}_x\text{C} \rightarrow \text{Li}_{1-x+dx}\text{CoO}_2 + \text{Li}_{x-dx}\text{C}$ for discharging, and $\text{Li}_{1-x+dx}\text{CoO}_2 + \text{Li}_{x-dx}\text{C} \rightarrow \text{Li}_{1-x}\text{CoO}_2 + \text{Li}_x\text{C}$ for charging. This is the transportation of lithium ions between the cathode and anode during charging and discharging.[6],[5]

C. SOURCE FOR TEST CELLS

The Sony US18650 graphite lithium-ion cells that are used in this research were obtained by dismantling Sony BP-GL95 Lithium-Ion Battery Packs. Each battery pack contained 12 individual cells. The procedure used for dismantling the battery packs can be found in Appendix A.

D. MANUFACTURE DATES

The last five letters and numbers of the individual cell's lot number provide the manufacture date of the cell. Due to the shelf life of lithium-ion cells, it is important to know if all of the cells being used in the battery were manufactured at the same time. Additionally, knowledge of the manufacture date will determine how long a battery can remain in storage and still be used. It will be shown in Chapter VIII that lithium-ion cells lose capacity while in storage. As time passes, the capacity of an individual cell will decrease as it ages, even without the cell being cycled. The last five letters and numbers of the lot number provide the manufacturing year, month, and day, as well as the electrode history. The code is listed in Table 1. [7]

Digit 1	Digit 2	Digit 3&4	Digit 5
Year	Month	Day	Electrode History
N = 2005	A = Jan	01	Α
O = 2006	B = Feb	02	В
P = 2007	C = Mar	03	С
	:	:	:
	:	:	:
	K = Nov	30	Υ
	L = Dec	31	Z

Table 1. Determination of manufacture date from lot number (After [7]).

Therefore, a lot number of "T 6B117OK28S" would be read as follows. From the last five digits of OK28S, we can determine the manufacture date as 28 November 2006 with electrode history S. This is the lot number on the 24 cells extracted from the first two battery packs. The last battery pack had cells with lot number "T 6B117OL26T". Therefore, these cells were manufactured on 26 December 2006 with electrode history T. At the present time, no research has been done at Naval Postgraduate School to determine differences between electrodes and their electrode histories have on cell capacity or characteristics.

III. CONTROL PROCEDURES

A. TEST PURPOSE

This procedure is the control for all short term testing done on the graphite lithium ion cells. Short term testing is defined as any testing that will be performed for less than 20 cycles. As a cell is cycled, its capacity decreases slightly with each cycle. This thesis contains tests which are designed to measure any capacity loss that occurs under circumstances not related to a cell being cycled. As a control, the following test was designed to identify this capacity loss so it can be accounted for in other tests.

For example, if results from a given test, in which capacity loss was to be measured without the effects of cycling, produced a reduction in capacity of 1.4%, and the cell had been cycled three times during this procedure, it could be interpreted that the circumstances of the test resulted in all the capacity loss. However, this would not take into effect the capacity loss due to the three cycles the cell performed during the test. Therefore, the reduction of capacity would be compared to the control procedure to determine the capacity loss (or gain) due to the test.

B. TEST METHOD

Each cycle charged the cells to 4.1 Volts and then discharged them to 100% Depth of Discharge (DOD), which for the US18650 Graphite Lithium-Ion Cell is 3.0 Volts. The charge rate of each test was the same as the discharge rate. The two rates used for this test is 0.35 Amps and 0.70 Amps. Each test was set up to perform the cycle 20 times. Each cycle was a measurement of the test cell's capacity, so no special provisions were made to perform a capacity measurement. All procedures were performed under a constant temperature of 25° C.

C. TEST OBJECT

The cells used for this test are Sony US18650 Graphite Lithium-Ion Cells. Cells used for this procedure were Naval Postgraduate School assigned serial numbers GT-001, GT-002, GT-003, GT-004, GT-005, and GT-006.

D. TEST EQUIPMENT AND SETUP

1. Equipment Used for Procedure

The equipment used for this procedure is the MACCOR battery test system described in Appendix B, a Thin-Line Series 80 parallel gap welder, model number 88F described in Appendix D, and a PolyScience Recirculator described in Appendix E.

2. Setup for Procedures

The recirculator was set to a temperature of 26° C, which maintained the tested cells at a constant temperature of 25° C. The cells for the test were selected and removed from the refrigerator. After allowing the cells approximately 30 minutes to come up to room temperature, solder tabs approximately two inches in length were welded on to the ends of the cells using the parallel gap welder. The cells were then wrapped in CHO-THERM, a thermally conductive, electrically isolating material which allows the temperature of the thermal plate to encompass the cell, thus providing good thermal contact and a more constant temperature throughout the cell. The cells were then placed on the thermal plate and covered with a custom fit bracket. The bracket was then screwed down to the plate to ensure the cells would not move throughout the procedure. The thermocouple was then slid in the gap between the cell and the bracket to a distance half way up the cell. The test leads were then connected to the corresponding solder tabs. After ensuring all alligator clips were tight, and the MACCOR software registered the cell's voltage, the lid was placed on the testing container and the procedure was ready to begin.

E. MACCOR TEST PROCEDURES

The MACCOR procedure for this test is listed in Appendix E. This appendix consists of the exact programming that is required for the MACCOR software to operate this procedure. The programming is in the form of a table, which is identical to the table displayed in the user interface by the software. It consists of individual steps, which are performed in order, and specify what the individual channel does at that point in the procedure.

F. TEST RESULTS

For each test, plots were produced that graph cell capacity per charge/discharge cycle as a percentage of the first capacity measurement. A graph of percentage capacity change versus cycle for a 0.35 Amp charge/discharge rate is shown in Figure 2. A graph of percentage capacity change versus cycle for a 0.70 Amp charge/discharge rate is shown in Figure 3.

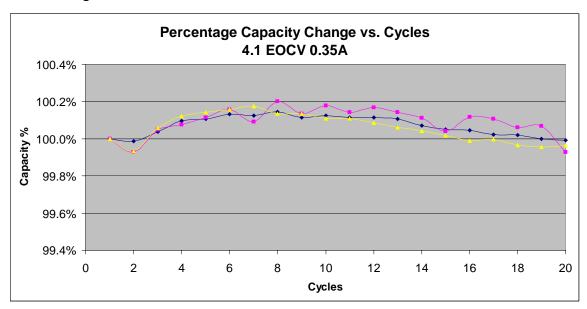


Figure 2. Percentage capacity change per cycle at a 0.35 Amp rate.

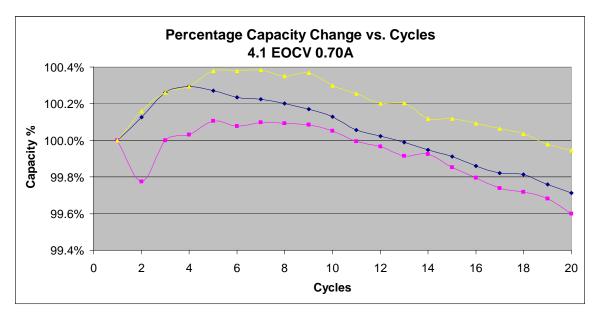


Figure 3. Percentage capacity change per cycle at a 0.70 Amp rate.

The total amount of capacity change was very small over the 20 cycles. For the 0.35 Amp rate, the change from maximum to minimum capacity was less than 0.3%. For the 0.70 Amp rate, the change from maximum to minimum capacity was less than 0.8%. To determine the trend as an average, the results of the three cells were averaged together. The graph of the average capacity loss for the 0.35 Amp rate is shown in Figure 4. The graph of the average capacity loss for the 0.70 Amp rate is shown in Figure 5.

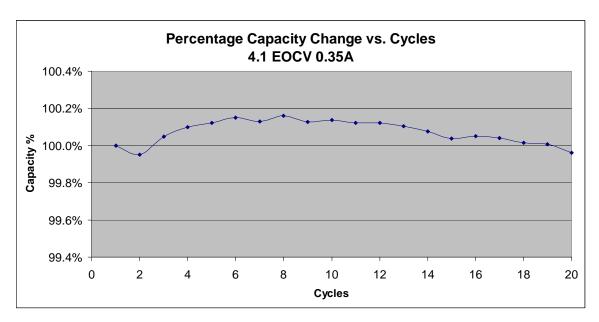


Figure 4. Average percentage capacity change per cycle at a 0.35 Amp rate.

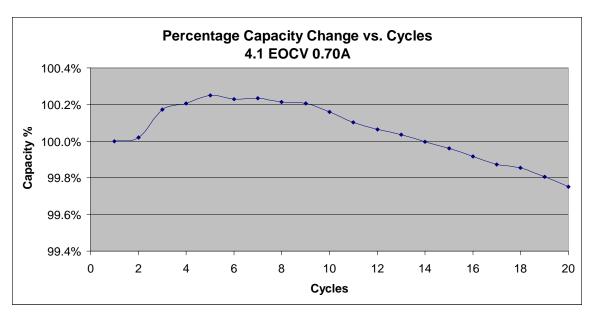


Figure 5. Average percentage capacity change per cycle at a 0.70 Amp rate.

The trend that was seen on both current rates was that the cells initially gained some capacity through the first six to eight cycles. After that, the cells started to slowly loose capacity as the cell cycled. The explanation for this trend would have to fall somewhere in the actual chemistry of the cell. As described earlier, the chemical reaction of the initial charge is different than the chemical reaction of the subsequent charge/discharge cycles. Therefore, a possible explanation for this result is that after the initial charge, the subsequent 10 to 20 charge cycles continue the chemical reaction of the initial charge.

With the ability to account for the capacity loss due to cycling, the rest of the procedures can by initiated. The relevant place to start is the first effect a battery would encounter on its trip to orbit, the launch.

IV. RANDOM VIBRATION TESTING

A. TEST PURPOSE

During the launching of a spacecraft, the ride is not smooth. The rocket and its contents are subjected to large vibrations at varying energies over a specified frequency range. A spacecraft must be built to withstand the riggers of the launch. Additionally, it must be known how different components, including the spacecraft battery, will respond to this vibration. The purpose of this test is to determine the effects, if any, vibrations similar to that experienced during a launch will have on cell capacity.

B. TEST METHOD

This test subjects cells to a random vibration test with a spectrum equal to the launch environment to measure capacity loss from vibration. This spectrum was obtained from Table 2.4-4 in the General Environmental Verification Specifications.[8] The spectrum as it was tested is listed in Table 2.

Step	Frequency	Acceleration	Slope Type	Alarm (dB)		Abort (dB)	
	(Hz)	(G ² /Hz)		Low	High	Low	High
1	20	0.026	+6dB/Oct	-3	3	-6	6
2	50	0.16	Slope	-3	3	-6	6
3	800	0.16	-6dB/Oct	-3	3	-6	6
4	2000	0.026	Slope	-3	3	-6	6

Table 2. Vibration spectrum for graphite cells (After [8]).

Vibration testing is performed on all three axes of the cell. The first axis vibrated is with the cell lying on its side, parallel to the floor. The second axis vibrated is the same as the first, except the cell is rotated around so that the axis that was parallel to the floor is now perpendicular to the floor. Finally, the third axis vibrated is with the cell standing on end, perpendicular to the floor. The procedure consists of forming two groups of three cells, which run through two full charge/discharge cycles (4.1 Volts to 3.0 Volts), with a capacity measurement being performed on the second discharge cycle. The first cycle is considered a break-in cycle for the cell. The groups of three were

chosen so that if there was a major discrepancy of data on one of the three cells, either due to a cell or test system failure, a characterization of the cells could still be gathered. Each group has a different charge/discharge current; the rates were 0.35 Amps and 0.70 Amps. The temperature was kept constant at 25° C. The cells then underwent random vibration testing on all three axes, with a capacity measurement being performed after each axis. The capacities were compared to the control group to see if there is any potential capacity loss due to the launch environment.

C. TEST OBJECT

The cells used for this test are Sony US18650 Graphite Lithium-Ion Cells. Cells used for this procedure were Naval Postgraduate School assigned serial numbers GT-013, GT-014, GT-015, GT-016, GT-017, and GT-018.

D. TEST EQUIPMENT AND SETUP

1. Equipment Used for Procedure

The equipment used for this procedure is the MACCOR battery test system described in Appendix B, a Thin-Line Series 80 parallel gap welder, model number 88F described in Appendix D, and a PolyScience Recirculator described in Appendix E. Vibration testing was accomplished by the use of a MB Dynamics Vibration Exciter PM500A.

2. Setup for Procedures

a. Setup for Capacity Measurement

The recirculator was set to a temperature of 26° C, which maintained the tested cells at a constant temperature of 25° C. The cells for the test were selected and removed from the refrigerator. After allowing the cells approximately 30 minutes to come up to room temperature, solder tabs approximately two inches in length were welded on to the ends of the cells using the parallel gap welder. The cells were then wrapped in CHO-THERM, attached to the thermal plate, and connected to the MACCOR system as described in Chapter III.

b. Setup for Vibration Procedure

For vibration testing, a clamp was previously manufactured to allow cells to be vibrated on all three axes. The clamp holds all six cells undergoing this procedure at one time. The first step is to ensure the ends of the cells are smooth. After removing the solder tabs from the cells with a pair of needle nose pliers, a Dremel rotary tool with a grinding stone is used to grind down cell ends smooth. At this time, a line is drawn on each cell with permanent marker running the length of the cell. This line is used to ensure that the cell is placed back in the clamp in correct position to ensure the cell is vibrated on all three of its axes as the clamp is rotated after each vibration. Two layers of Kapton tape were then applied perpendicular to each other on each end of the cell to provide a tight fit in the clamp and prevent the cell from shorting out through the clamp during vibration. The clamp was secured with four screws to hold the cells in place. Another plate was then secured to the clamp with six screws for added stability and for attaching the clamp assembly to the vibration table. The clamp assembly was then attached to the top of the vibration table with six bolts. The assembly is positioned so that the axis to be vibrated is vertical as the head of the vibration table vibrates. A picture of the proper configuration and mounting of the clamp is shown in Figure 6.

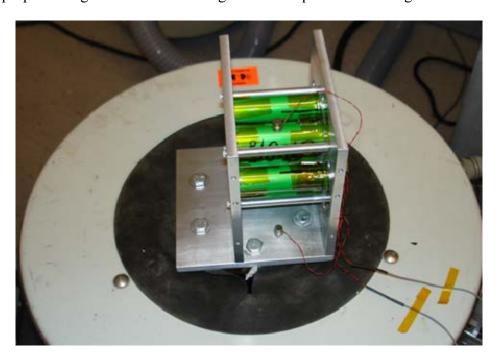


Figure 6. Picture of cells clamped for vibration testing.

E. MACCOR TEST PROCEDURES

The MACCOR procedure for this test is listed in Appendix G.

F. TEST RESULTS

The following tables list the cell capacities after the first two cycles, with the second cycle being considered the initial capacity. The tables then list the capacities of each cell after vibration was performed on an axis. Each cell then shows a percentage change between the two capacity checks. The capacities at a current of 0.35 Amps are listed in Table 3. The capacities at a current of 0.70 Amps are listed in Table 4.

	1st Cell	1st Cell %	2nd Cell	2nd Cell %	3rd Cell	3rd Cell %
Break-in Capacity	1.88134	0.0000%	1.88549	0.0000%	1.88956	0.0000%
Initial Capacity	1.88081	-0.0282%	1.88581	0.0168%	1.89143	0.0991%
After 1st Axis	1.91272	1.6680%	1.91977	1.8183%	1.92169	1.7003%
After 2nd Axis	1.90545	1.2815%	1.90958	1.2775%	1.91511	1.3523%
After 3rd Axis	1.90678	1.3524%	1.91292	1.4550%	1.91555	1.3751%

Table 3. Capacity for vibration at a 0.35 Amp rate.

	1st Cell	1st Cell %	2nd Cell	2nd Cell %	3rd Cell	3rd Cell %
Break-in Capacity	1.70446	0.0000%	1.70627	0.0000%	1.70232	0.0000%
Initial Capacity	1.70950	0.2956%	1.71115	0.2858%	1.70601	0.2168%
After 1st Axis	1.75094	2.7271%	1.74986	2.5548%	1.74425	2.4633%
After 2nd Axis	1.74783	2.5446%	1.75083	2.6115%	1.74128	2.2886%
After 3rd Axis	1.74648	2.4651%	1.74958	2.5380%	1.74128	2.2886%

Table 4. Capacity for vibration at a 0.70 Amp rate.

The capacity change seen in this data correlates with the trend seen in the control procedure data in which a smaller change in capacity is observed at the lower the charge/discharge rate. How much of the capacity change is due to vibration and how much is due to the cycling of the cell is described below.

The following tables compare the average capacity change recorded after each axis is vibrated to the average capacity change seen in the control group. Through these tables, the comparison can be made to see if the effects of launch vibrations will have an affect on the cells. The average percentage column shows the percentage of capacity

change with respect to the initial capacity measurement. The averages at a current rate of 0.35 Amps are listed in Table 5. The averages at a current rate of 0.70 Amps are listed in Table 6.

Te	Control Cells				
	<u>Average</u>	Average %		<u>Average</u>	Average %
Break-in Capacity	1.88546	0.0000%	1st Cycle	1.87953	0.0000%
Initial Capacity	1.88602	0.0293%	2nd Cycle	1.87859	-0.0500%
After 1st Axis	1.91806	1.7289%	3rd Cycle	1.88043	0.0482%
After 2nd Axis	1.91005	1.3038%	4th Cycle	1.88139	0.0989%
After 3rd Axis	1.91175	1.3942%	5th Cycle	1.88180	0.1210%

Table 5. Average capacity for vibration at a 0.35 Amp rate.

Те	Control Cells				
	<u>Average</u>	Average %		<u>Average</u>	Average %
Break-in Capacity	1.70435	0.0000%	1st Cycle	1.70551	0.0000%
Initial Capacity	1.70888	0.2661%	2nd Cycle	1.70585	0.0200%
After 1st Axis	1.74835	2.5818%	3rd Cycle	1.70846	0.1729%
After 2nd Axis	1.74665	2.4817%	4th Cycle	1.70903	0.2061%
After 3rd Axis	1.74578	2.4307%	5th Cycle	1.70980	0.2511%

Table 6. Average capacity for vibration at a 0.70 Amp rate.

To easily compare the capacity change after vibration, graphs were produced to visually show the results of the above listed data. The graph of average capacity for vibration at a 0.35 Amp rate is shown in Figure 7. The graph of average capacity for vibration at a 0.70 Amp rate is shown in Figure 8.

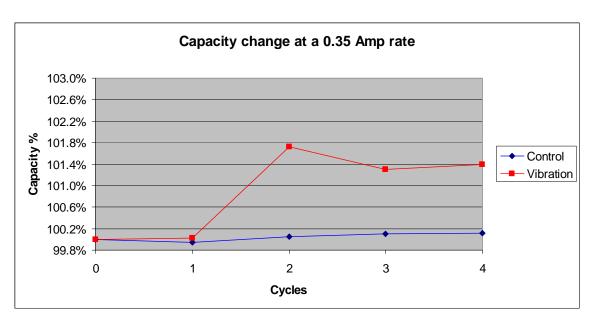


Figure 7. Average capacity for vibration at a 0.35 Amp rate.

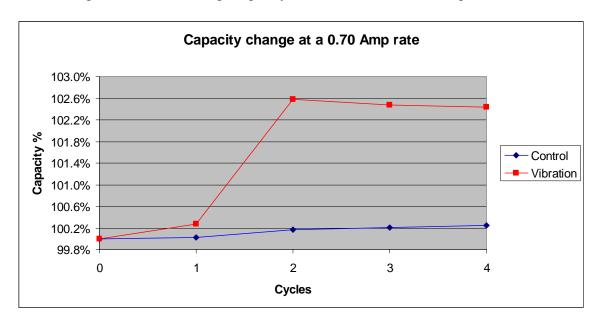


Figure 8. Average capacity for vibration at a 0.70 Amp rate.

It is interesting to note that for all procedures, the capacity of all cells increased significantly after the first axis of the cells was vibrated. While the cells in the control procedure also showed some slight increase in capacity, the cells that were being vibrated showed a much larger change after being vibrated as compared to the control cells which were not vibrated. This change was over a percentage point higher for the 0.35 Amp rate,

and over two percentage points higher for the 0.70 Amp rate. A possible explanation for this effect is that the vibration from the procedure may more thoroughly mix the electrolyte solution. Longer term testing on these cells would be required to see if this increase in capacity was permanent or merely a short term effect.

If a set of cells was to undergo vibration testing, and then placed into a LEO simulated procedure as described in Chapter VIII, the results of this LEO simulation could be compared to a LEO simulation that did not undergo vibration testing over an extended period of time. By comparing the results of these two procedures, it could be determined if this increase in capacity is permanent or short term. Either way, based on the results of this procedure, it appears as though the vibrations these cells would receive during a launch would slightly increase the cell capacity.

Knowing how the cell will handle the launch environment is the first of many characteristics that is required. The next item that is needed is to determine what effect temperature has on the capacity of a cell.

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V. CELL CAPACITY VERSUS TEMPERATURE

A. TEST PURPOSE

This test will consist of gathering data to build a family of curves that will specify the expected available cell capacity versus temperature for graphite cells. The procedure begins by forming two groups of three cells, which will be put through a break-in procedure of one full charge/discharge cycle to get an initial capacity measurement. The cells will then go through procedures where they are discharged at constant current from 4.1 Volts down to 3.0 Volts. This procedure will be repeated every five degrees from 5° C to 40° C. This test will be repeated at currents of 0.35 Amps and 0.70 Amps. These charge/discharge rates were chosen to allow for comparison with the results from a previous thesis on hard carbon lithium-ion cells.[3] The results will then be graphed as a family of curves.

B. TEST METHOD

This procedure charges the graphite cells to 4.1 Volts, rests for 10 minutes to allow the cells to drift to a stable starting point, and then discharges them to 3.0 Volts. The cycle is performed at 5° C increments from 5° C to 40° C. The charge rate of each test is the same as the discharge rate. The rates used for these tests were 0.35 Amps and 0.70 Amps.

C. TEST OBJECT

The cells used for this test are Sony US18650 Graphite Lithium-Ion Cells. Cells used for this procedure were Naval Postgraduate School assigned serial numbers GT-019, GT-020, GT-021, GT-022, GT-023, and GT-024.

D. TEST EQUIPMENT AND SETUP

1. Equipment Used for Procedure

The equipment used for this procedure is the MACCOR battery test system described in Appendix B, a Thin-Line Series 80 parallel gap welder, model number 88F described in Appendix D. Temperature was controlled through a PolyScience Recirculator described in Appendix E.

2. Setup for Procedures

The recirculator was set to a temperature of 5° C, which maintained the tested cells at a constant temperature of 5° C. The cells for the test were selected and removed from the refrigerator. After allowing the cells approximately 30 minutes to come up to room temperature, solder tabs approximately two inches in length were welded on to the ends of the cells using the parallel gap welder. The cells were then wrapped in CHO-THERM, attached to the thermal plate, and connected to the MACCOR system as described in Chapter III. At the completion of each procedure, the recirculator temperature setting was increased by 5° C. After allowing the temperature to equalize for 30 minutes, the temperature of the cells was checked on the MACCOR system. Small adjustments of 0.5° C were then made to the recirculator to get the thermal plate to the required temperature.

E. MACCOR TEST PROCEDURES

The MACCOR procedures for this test are listed in Appendix H.

F. TEST RESULTS

The following figures (Figure 9 – Figure 14) show the family of curves for all six cells that were used in this procedure. Of interest is that the curves are quite flat throughout the discharge cycle. This shows that the cells maintain a fairly constant voltage throughout the discharge cycle. This is an advantage of the graphite cells over the hard carbon cells, whose discharge curve has much more of a slope during discharge.

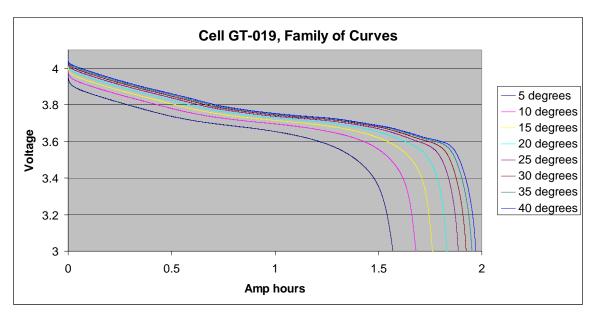


Figure 9. Family of curves for cell GT-019 at a 0.35 Amp rate.

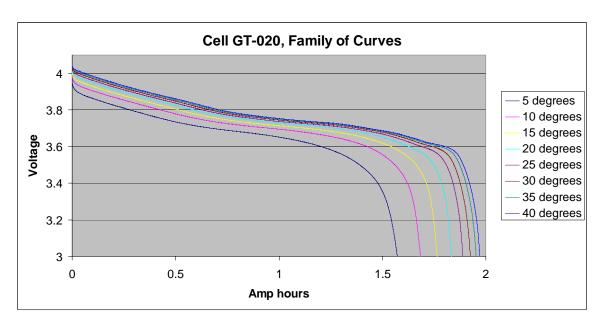


Figure 10. Family of curves for cell GT-020 at a 0.35 Amp rate.

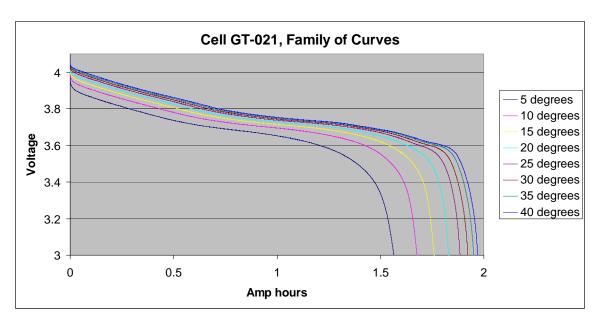


Figure 11. Family of curves for cell GT-021 at a 0.35 Amp rate.

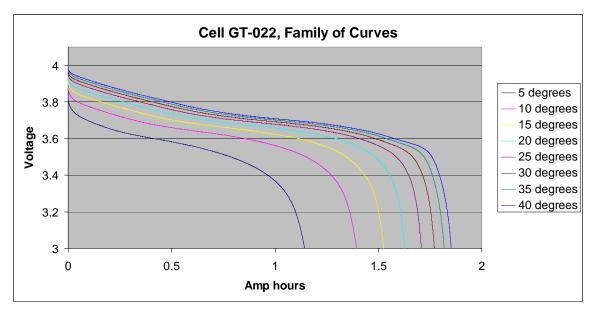


Figure 12. Family of curves for cell GT-022 at a 0.70 Amp rate.

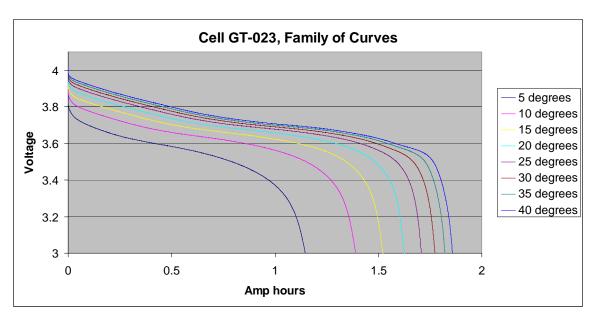


Figure 13. Family of curves for cell GT-023 at a 0.70 Amp rate.

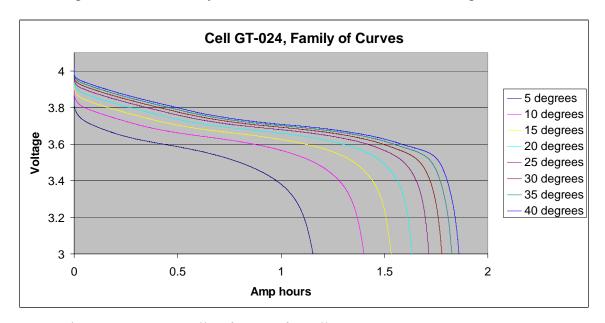


Figure 14. Family of curves for cell GT-024 at a 0.70 Amp rate.

A comparison of total cell capacity versus the temperature at which the capacity measurement was taken is shown in Figure 15. The graph has been normalized to 40° C. The cell capacity increases with temperature. Additionally, the capacity difference for the lower discharge rate is much less than the higher discharge rate over the given temperature range.

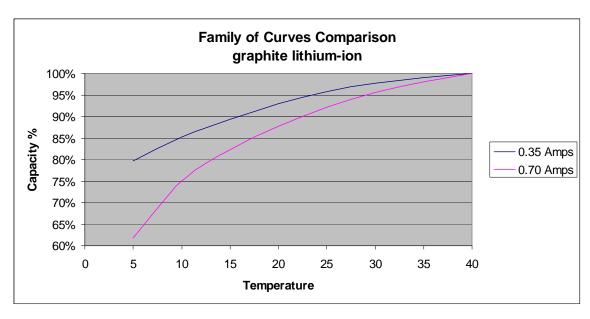


Figure 15. Graphite family of curves comparison.

Based on the family of curves data, some interesting observations are noted. First, the higher the temperature during the discharge cycle, the more capacity the cell has. However, maintaining a battery at 40° C on a spacecraft is not realistic as the power requirement for a heater would be more than what is gained by a higher capacity. Another observation is that the lower the discharge rate, the less the capacity decreases due to temperature effects. These two observations lead to the conclusion that a battery comprised of graphite lithium-ion cells can be very effective and very flexible. By varying the number of strings in a battery to keep the individual cell current around 0.35 Amps, a battery can be designed to stay very near its maximum capacity with little requirement to keep the battery warm. Even at 5° C, a cell still has almost 80% of its maximum capacity available. If that temperature is raised just 10°, to 15° C, a cell will be able to provide almost 90% of its maximum capacity.

Comparing these results of the graphite cells to hard carbon cells shows that the graphite cells are much more consistent than hard carbon. That is, over a large range of temperatures, the graphite cells variation in capacity and discharge curves is notably less than the hard carbon cells. A graph of a family of curves using data from a previous thesis on hard carbon cells can be seen in Figure 16. [3]

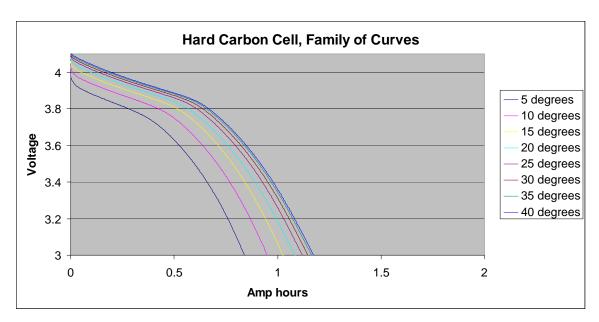


Figure 16. Family of curves for a hard carbon cell at a 0.35 Amp rate (After [3]).

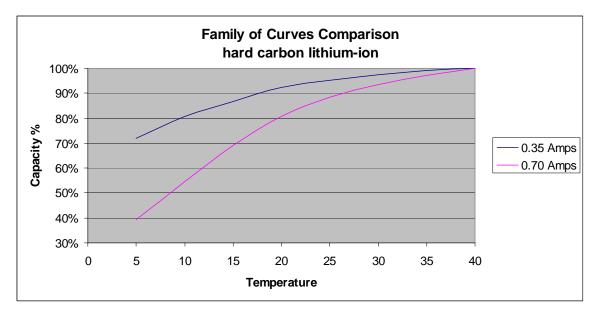


Figure 17. Hard carbon family of curves comparison (After [3]).

The curve is not as flat as graphite cells during the discharge cycle. Thus, the hard carbon cell does not maintain a consistent discharge rate throughout the discharge cycle. Additionally, even though the hard carbon cell does not reach 100% DOD until 2.5 Volts, the capacity of the graphite cell is far superior. At 40° C, the capacity

percentage of the graphite cell is 65% more than the capacity of the hard carbon cell. The effects of temperature on the hard carbon cell is also much more than the graphite cell. The hard carbon cells lose as much as 60% of their maximum capacity at a discharge current of 0.70 Amps at 5° C as shown in the graph in Figure 17. This compared to the graphite cells which only lose just fewer than 40% of their maximum capacity at a discharge current of 0.70 Amps at 5° C.

The comparisons listed above do show how the graphite cell is much better than the hard carbon regarding capacity. However, to make a precise comparison, one must look at the capacity differences in relation to the C rating. The C rating of a cell is nothing more than its rated capacity at a given current. Assume a cell with a capacity of 1.5 Amp hours is desired to be discharged at C/2. This would be in a current of 0.75 Amps. Graphite cells have a much higher capacity than the hard carbon cells, which results in a higher C rating per cell. Using data from this thesis and a prior thesis on hard carbon cells [3], a current of 0.70 Amps is C/2.4 for the graphite and C/1.4 for the hard carbon. To precisely compare the two cells, data would have to be obtained in which both hard carbon and graphite cells were being discharged at the same current as compared to their C rating.

Another aspect of the graphite cells is their voltage drift upon completion of a charge or discharge cycle. It needs to be discovered if this drift is something that should be taken into account when matching cells for a battery.

VI. VOLTAGE DRIFT

A. TEST PURPOSE

At the completion of a charge or discharge cycle, the open circuit voltage of an individual cell will not maintain its exact voltage. When a cell is charging, the voltage is steadily increasing. When the charging is stopped, the cell voltage will immediately relax. Additionally, when a cell is discharging, the voltage is steadily decreasing. When the discharging is stopped, the cell voltage will immediately rebound. This test is designed to find out how much the cell voltage will drift at the end of a charge or discharge cycle, and if it needs to be included as a factor when matching cells for a battery comprised of graphite lithium-ion cells. Ideally, the cells in a particular string will have identical voltages. Thus, when the string is charging, the cells will all reach their end of charge voltage (EOCV) at the same time and, thus, provide the maximum string capacity. If the cells in a particular string drift to different voltages at the end of a discharge cycle, their voltages may not stay together during the subsequent charge cycle. If the string is being charged to a total string voltage, some of the cells could be overcharged. Additionally, if the cells drift to different voltages at the end of a charge cycle, their voltages will not stay together during the subsequent discharge cycle. This could possibly lead to a cell being discharged below 100% DOD as the string discharges. Over time, the cells could drift further and further apart, reducing the overall capacity in the string. In a worst case, this could destroy one or more cells in the string, destroying the string and reducing the overall battery capacity by the capacity of the failed string.

B. TEST METHOD

This procedure measures the amount of a cell's voltage drift at the completion of both a full charge and full discharge cycle. The voltage drift at the end of the charge or discharge cycle was determined from the open circuit voltage at the end of the cycle and the voltage following a 30-minute rest. The voltage drift at the end of the charge cycle was conducted during the control procedure. At the conclusion of the control procedure, the cells were charged until they reached their EOCV of 4.1 Volts; they were allowed to

rest for a period of 30 minutes, with data being collected every second. The procedure to determine the voltage drift at the end of the discharge cycle was a separate procedure. After first charging the cells to an EOCV of 4.1 Volts, the cells were allowed to discharge until they reached their end of discharge voltage (EODV) of 3.0 Volts. They were then allowed to rest for 30 minutes, with data being collected every second. All procedures were performed under a constant temperature of 25° C. The rates used for these tests were 0.35 Amps and 0.70 Amps.

C. TEST OBJECT

The cells used for this test are Sony US18650 Graphite Lithium-Ion Cells. Cells used for this procedure NPS assigned were serial numbers GT-001, GT-002, GT-003, GT-004, GT-005, and GT-006.

D. TEST EQUIPMENT AND SETUP

1. Equipment Used for Procedure

The equipment used for this procedure is the MACCOR battery test system described in Appendix B, a Thin-Line Series 80 parallel gap welder, model number 88F described in Appendix D, and a PolyScience Recirculator described in Appendix E.

2. Setup for Procedures

The recirculator was set to a setting of 26° C, which maintained the tested cells at a constant temperature of 25° C. The cells for the test were selected and removed from the refrigerator. After allowing the cells approximately 30 minutes to come up to room temperature, solder tabs approximately two inches in length were welded on to the ends of the cells with the parallel gap welder. The cells were then wrapped in CHO-THERM, attached to the thermal plate, and connected to the MACCOR system as described in Chapter III.

E. TEST PROCEDURES

The procedures for this test are listed in Appendix I.

F. TEST RESULTS

For each procedure, graphs were produced that showed voltage drift of each cell. Voltage drift over time at a 0.35 Amp rate after charging is shown in Figure 18. Voltage drift over time at a 0.70 Amp rate after charging is shown in Figure 19. Approximately 90% of the voltage drift occurs during the first five minutes after the charge stops. The remaining 10% of the measured voltage drift occurs over the remaining 25 minutes. The voltage drift is greater in the 0.70 Amp rate than in the 0.35 Amp rate. At the end of the charge cycle, the average voltage drift of the three cells for the 0.35 Amp rate after 30 minutes was 0.056 Volts, and the average voltage drift of the three cells for the 0.70 Amp rate after 30 minutes was 0.106 Volts. It can be seen for the 0.70 Amp rate, there is a slight separation in the voltage drift. This separation correlates to a small difference in the capacities of the individual cells. The cell which drifted slightly lower had 4 to 5 mAmp hours more capacity than the other two cells.

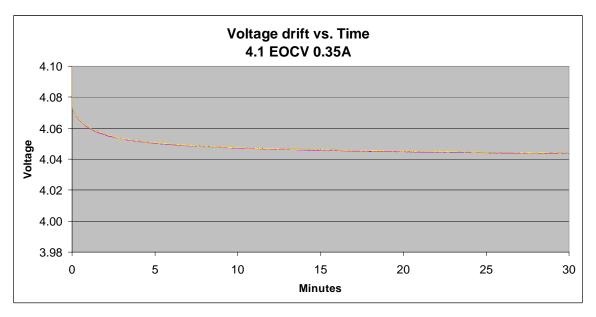


Figure 18. Voltage drift over time at a 0.35 Amp rate after charging.

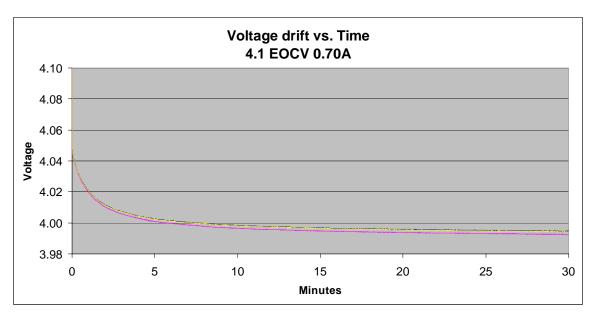


Figure 19. Voltage drift over time at a 0.70 Amp rate after charging.

The two graphs below show the voltage drift at the end of a discharge cycle. Voltage drift over time at a 0.35 Amp rate after discharging is shown in Figure 20. Voltage drift over time at a 0.70 Amp rate after discharging is shown in Figure 21. It was noted, unlike the voltage drift after charging, that around 90% of the measured voltage drift occurs during the first fifteen minutes after the discharge stops for the 0.35 Amp rate. Additionally, at the 0.70 Amp rate, around 90% of the measured voltage drift occurs during the first ten minutes after the discharge stops. The voltage drift is greater in the 0.70 Amp rate than in the 0.35 Amp rate. At the end of the discharge cycle, the average voltage drift of the three cells for the 0.35 Amp rate after 30 minutes was 0.393 Volts, and the average voltage drift of the three cells for the 0.70 Amp rate after 30 minutes was 0.533 Volts. Additionally, there is a direct correlation between the amount of drift separation seen at the 0.35 Amp rate and the cell capacity. The cell which drifted slightly higher had a capacity 4 to 5 mAmp hours less than the other two cells. However, is it also interesting to note that the voltage drift seen at the 0.70 Amp rate had a maximum difference of 1.2 mVolts between the three cells, but the capacity of one of the cells was almost 8 mAmp hours less than the other two.

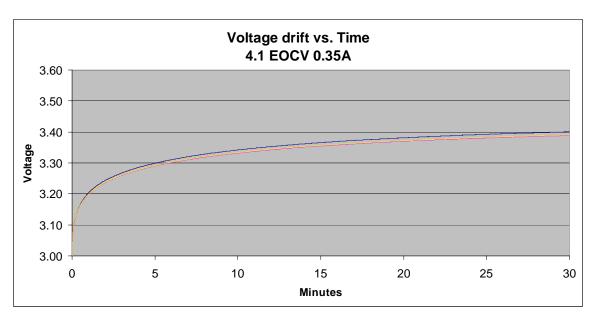


Figure 20. Voltage drift over time at a 0.35 Amp rate after discharging.

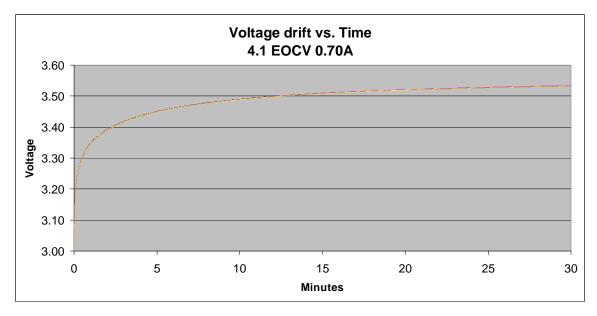


Figure 21. Voltage drift over time at a 0.70 Amp rate after discharging.

It is apparent that cell drift is not a factor in matching cells for a battery. The differences between the cells after drifting from a full charge were less than 1 mVolt for the 0.35 Amp charge rate, and less than 2 mVolts for the 0.70 Amp charge rate. Cell drift after a full discharge was slightly different, with the difference between the cells after

drifting from a full discharge were just over 10 mVolts for the 0.35 Amp discharge rate, and just over 1 mVolt for the 0.70 Amp discharge rate. This difference in voltage after drifting is negligible and is not large enough of a factor to affect the cells in a string. While the 10 mVolt difference in the 0.35 Amp discharge rate is much larger than the other results, it should not be enough of a factor to affect the battery as a whole. Additionally, the battery on a spacecraft is never going to be discharged to 100% DOD unless there is a problem onboard. The most important drift factor is the drift after full charge, which has been noted as negligible between cells. While some correlation was seen between capacity and the amount of drift separation, there was an equal amount of results in which the voltage drift had no separation, yet the capacities were different. This leads to the conclusion that voltage drift cannot be predicted based on a cell's capacity.

As the operational characteristics of graphite lithium-ion cells are understood, another characteristic is also required. This is an understanding of how long a cell can be stored while still maintaining a useful level of capacity. Loss of capacity while in storage is a big factor when determining when to purchase a spacecraft battery. Additionally, if a spacecraft launch is delayed, the knowledge of capacity loss in storage will contribute to the decision of whether to replace the battery or not prior to launch.

VII. CAPACITY LOSS IN STORAGE FOR HARD CARBON CELLS

A. TEST PURPOSE

The purpose of this test is to determine how much capacity a lithium-ion cell will lose while in storage. A capacity measurement performed 25 January 2007, on some graphite cells that were manufactured on 29 November 2003, showed a capacity significantly less than the rated capacity. These cells had been in storage at Naval Postgraduate School and had never been cycled. This discovery led to the requirement to understand capacity loss in storage. However, insufficient data to accurately measure this loss in the graphite cells is available as this data would need to be obtained over a number of months to years. Therefore, this section of the thesis is from data obtained over an 18-month period from hard carbon lithium-ion cells. It is assumed that data from the hard carbon cells will provide a general idea of how the graphite cells will react.

B. TEST METHOD

The hard carbon lithium-ion cells were first extracted from Sony BP-945 camcorder battery packs in January 2006. An initial capacity measurement was taken on all cells in February 2006, and a number of them remained in storage in the refrigerator at approximately 0° C. After over a year and a half in storage, a capacity measurement was performed on three of these cells. It was determined that these cells had lost capacity while in storage, without ever being cycled. A capacity measurement was then performed on these cells on a monthly basis to obtain data points. The capacity measurement is performed by charging the cells to 4.2 Volts, allowing them to rest for one minute, and then discharging them to 2.5 Volts. This one minute rest period was used in February 2006 during the initial capacity measurements; it was incorporated in the later tests to ensure consistency of the capacity measurement. The charge rate of each test was the same as the discharge rate. The rate used for this test was 0.375 Amps. All procedures were performed under a constant temperature of 25° C.

C. TEST OBJECT

The cells used for this test are Sony US18650 Hard Carbon Lithium-Ion Cells. Cells used for this procedure were Naval Postgraduate School assigned serial numbers 084, 087, and 116.

D. TEST EQUIPMENT AND SETUP

1. Equipment Used for Procedure

The equipment used for this procedure is the MACCOR battery test system described in Appendix B, a Thin-Line Series 80 parallel gap welder, model number 88F described in Appendix D, and a PolyScience Recirculator described in Appendix E.

2. Setup for Procedures

The recirculator was set to a temperature of 26° C, which maintained the tested cells at a constant temperature of 25° C. The cells for the test were selected and removed from the refrigerator. After allowing the cells approximately 30 minutes to come up to room temperature, solder tabs approximately two inches in length were welded on to the ends of the cells using the parallel gap welder. The cells were then wrapped in CHO-THERM, attached to the thermal plate, and connected to the MACCOR system as described in Chapter III.

E. TEST PROCEDURES

The MACCOR procedure for this test is listed in Appendix J.

F. TEST RESULTS

Graphs were created to show the amount of capacity loss over time. The graph showing each cell's capacity loss over time individually is shown in Figure 22. To provide an average capacity loss over time, the capacity measurements of the three cells were averaged together and are shown in Figure 23.

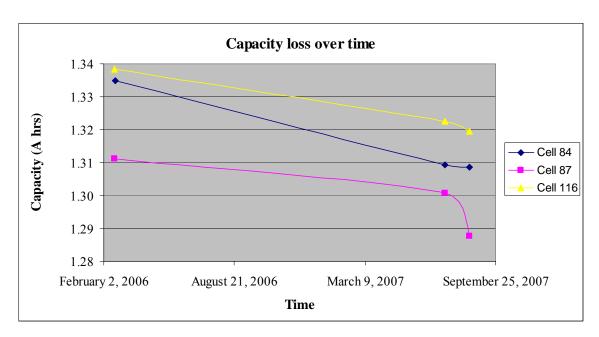


Figure 22. Capacity loss while in storage.

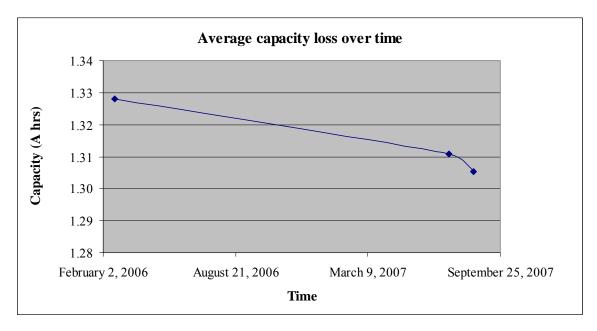


Figure 23. Average capacity loss while in storage.

While it was determined that the cells did indeed lose capacity while in storage, the actual amount of capacity loss was minimal. On average, the cells only lost 1.72% of their initial capacity over the 18-month span. This is very important to know as it will

effect when the cells for a spacecraft should be purchased. With such a small capacity loss while in storage at approximately 0° C, it would be possible to purchase the cells over a year prior to launch; and they would still have over 98% of their initial capacity available come launch.

VIII. LOW EARTH ORBIT SIMULATION

A. TEST PURPOSE

The purpose of this test is to determine the capacity loss over time of Sony graphite lithium-ion cells in a LEO orbit.

B. TEST METHOD

This test simulates a LEO orbit, which is 60 minutes sunlight and 30 minutes eclipse. This test cycles the cells on a 60-minute charge, 30-minute discharge cycle. The discharge rate of each test is twice the charge rate. The charge rates used for these tests are 0.25 Amps and 0.375 Amps, which were chosen based on expected rates on orbit. If a voltage of 4.1V is obtained prior to the 60-minute charge timeframe, the cell will go into a rest state for the remainder of the 60 minutes. This scheme simulates how the battery is charged on orbit. This is to avoid trickle charging the cell. Trickle charging is when a cell is charged at the same rate as the cell's self discharge rate, thus maintaining a fully charged battery.[9] Trickle charging will destroy a lithium-ion cell, so it must be avoided. After every 199th cycle of the initial test, the cell is charged to 4.1 Volts and then discharged to 3.0 Volts to provide a capacity measurement, and then charged back to 4.1 Volts to provide a uniform starting condition for the test. A current of 0.375 Amps was chosen for all capacity measurements to provide a common baseline for all capacity tests. All procedures were performed under a constant temperature of 25° C.

C. TEST OBJECT

The cells used for this test are Sony US18650 Graphite Lithium-Ion Cells. Cells used for this procedure were Naval Postgraduate School assigned serial numbers GT-025, GT-026, GT-027, GT-031, GT-032, and GT-033.

D. TEST EQUIPMENT AND SETUP

1. Equipment Used for Procedure

The equipment used for this procedure is the MACCOR battery test system described in Appendix B, a Thin-Line Series 80 parallel gap welder, model number 88F described in Appendix D, and a PolyScience Recirculator described in Appendix E.

2. Setup for Procedures

The recirculator was set to a temperature of 26° C, which maintained the tested cells at a constant temperature of 25° C. The cells for the test were selected and removed from the refrigerator. After allowing the cells approximately 30 minutes to come up to room temperature, solder tabs approximately two inches in length were welded on to the ends of the cells using the parallel gap welder. The cells were then wrapped in CHO-THERM, attached to the thermal plate, and connected to the MACCOR system as described in Chapter III.

E. TEST PROCEDURES

The MACCOR procedure for this test is listed in Appendix K.

F. TEST RESULTS

For each procedure, graphs were produced that showed the capacity loss versus the total number of cycles. At the time the last data was collected for this thesis, all cells had completed just over 2000 cycles, which equates to just over four months of orbit simulation. As can be seen from Figures 24 and 25, the cells at both charge rates are steadily losing capacity as the cell cycles. The cells being charged at the 0.250 Amp rate have lost only approximately 7% of their capacity, compared to the cells being charged at the 0.375 Amp rate, which have lost approximately 11% of their capacity. This correlates with results seen in the control procedure, in which cells cycled at lower current rates lost less capacity per cycle.

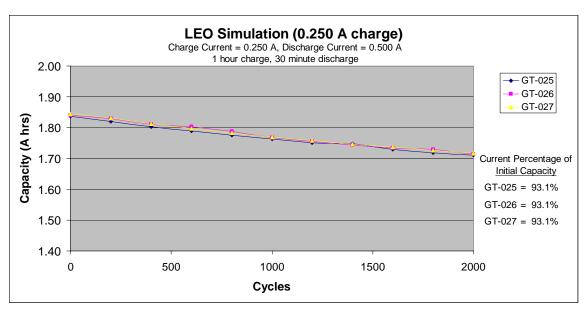


Figure 24. Capacity loss versus number of cycles at a 0.250 Amp charge rate in a LEO simulated orbit.

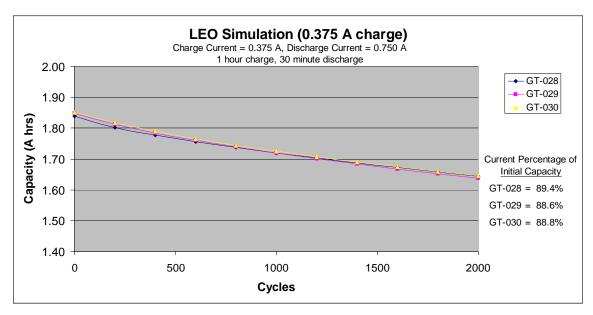


Figure 25. Capacity loss versus number of cycles at a 0.375 Amp charge rate in a LEO simulated orbit.

If this trend were to continue on in a linear fashion, it can be estimated that the cells will lose all their capacity after approximately five years, or approximately 29,000 cycles. This estimate was arrived at by taking the average capacity loss between each of

the 200 cycles and extrapolating it out over time. This result can only be verified by actually allowing the cells to cycle until their capacity completely runs out. If the previous estimate is correct, it will take approximately five years of testing to provide a definite answer.

A potential method to predict capacity loss in a shorter period of time is a process referred to as accelerated testing. In this process, the same power per cycle is charged and discharged in the cell. However, the time is shortened so that, in theory, one can see results of five years of testing in two and one-half years.

IX. ACCELERATED LOW EARTH ORBIT SIMULATION

A. TEST PURPOSE

The purpose of this test is to determine the viability of using accelerated testing to reduce the time required for cell testing. The theory behind the accelerated testing is as follows: A standard LEO satellite spends approximately one hour in the sun (charging), and 30 minutes in eclipse (discharging). A real time LEO simulation with a discharge rate of 1 Amp would have a charge rate of 0.5 Amps. To accelerate this test, the time to charge or discharge is halved, to give 30 minutes of charging, and 15 minutes of discharging. Additionally the amount of current is doubled to 2 Amps discharging and 1 Amp charging.[10] The theory follows that since it is the same amount of power in and out over the given cycle, 10 years of data can be generated in five years. This test will verify if this theory is valid.

B. TEST METHOD

This test simulates a LEO orbit, which is 60 minutes sunlight and 30 minutes eclipse. This test cycles the cells on a 30-minute charge, 15-minute discharge cycle. The discharge rate of each test is twice the charge rate. The charge rates used for these tests are 0.50 Amps and 0.75 Amps, which are twice the rates on the non-accelerated LEO simulation. If a voltage of 4.1V is obtained prior to the 30-minute charge timeframe, the cell will go into a rest state for the remainder of the 30 minutes. This is to avoid trickle charging and simulate how the spacecraft would operate on orbit. After every 199th cycle of the initial test, the cell is charged to 4.1 V and then discharged to 3.0 V to provide a capacity measurement, and then charged back to 4.1 V to provide a uniform starting condition for the test. A current of 0.375 Amps was chosen for all capacity measurements to provide a common baseline. All procedures were performed under a constant temperature of 25° C.

C. TEST OBJECT

The cells used for this test are Sony US18650 Graphite Lithium-Ion Cells. Cells used for this procedure were serial numbers GT-028, GT-029, GT-030, GT-034, GT-035 and GT-036.

D. TEST EQUIPMENT AND SETUP

1. Equipment Used for Procedure

The equipment used for this procedure is the MACCOR battery test system described in Appendix B, a Thin-Line Series 80 parallel gap welder, model number 88F described in Appendix D, and a PolyScience Recirculator described in Appendix E.

2. Setup for Procedures

The recirculator was set to a temperature of 26° C, which maintained the tested cells at a constant temperature of 25° C. The cells for the test were selected and removed from the refrigerator. After allowing the cells approximately 30 minutes to come up to room temperature, solder tabs approximately two inches in length were welded on to the ends of the cells using the parallel gap welder. The cells were then wrapped in CHO-THERM, attached to the thermal plate, and connected to the MACCOR system as described in Chapter III.

E. TEST PROCEDURES

The MACCOR procedure for this test is listed in Appendix K.

F. TEST RESULTS

For each procedure, graphs were produced that showed the capacity loss over the number of total cycles. The capacity loss over time of the cells being cycled at a 0.5 Amp charge rate, which is equivalent to the test being cycled at a 0.25 Amp charge rate from the previous chapter, only accelerated, is shown in Figure 26. The capacity loss over time of the cells being cycled at a 0.75 Amp charge rate, which is equivalent to the test being cycled at a 0.375 Amp charge rate from the previous chapter, only accelerated, is shown in Figure 27. Graphs comparing the accelerated and non-accelerated results can

be found in Figures 28 through 31. The comparison is capacity loss over the total number of cycles and capacity loss over total test time.

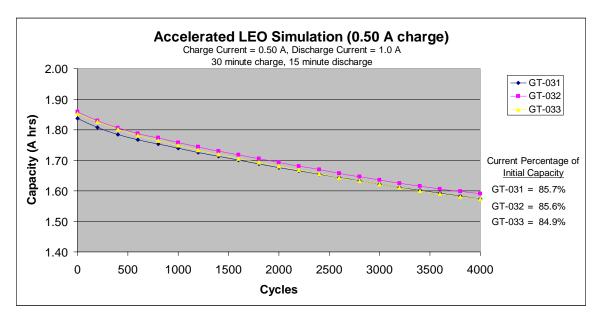


Figure 26. Capacity loss versus number of cycles at a 0.50 Amp charge rate in an accelerated LEO simulated orbit.

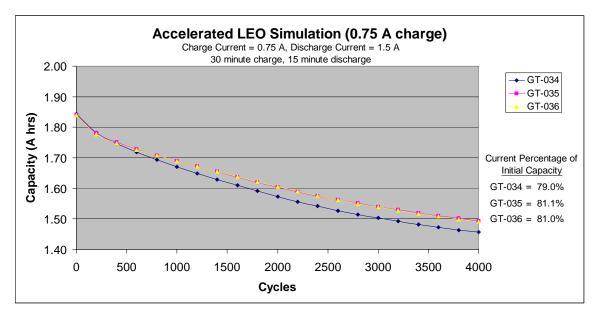


Figure 27. Capacity loss versus number of cycles at a 0.75 Amp charge rate in an accelerated LEO simulated orbit.

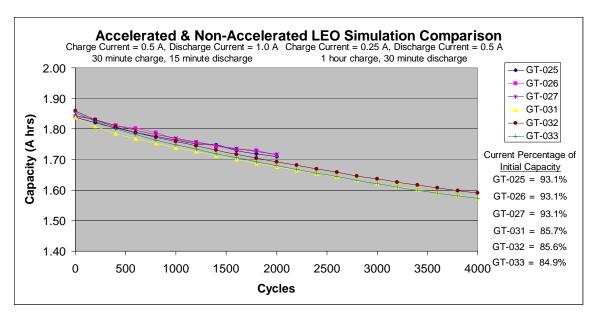


Figure 28. Comparison of accelerated and non-accelerated capacity loss versus number of cycles.

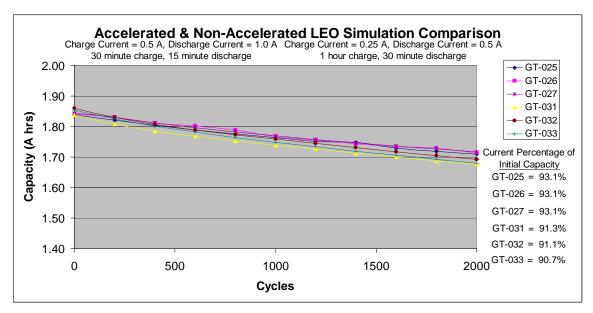


Figure 29. Comparison of accelerated and non-accelerated capacity loss versus number of cycles.

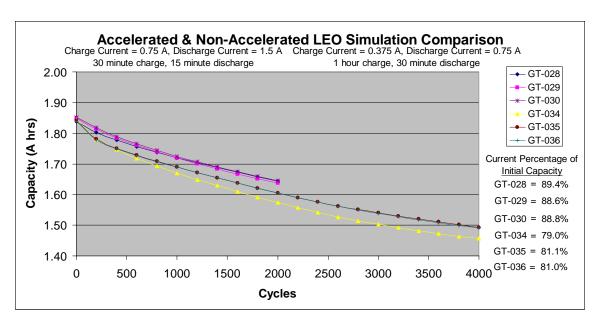


Figure 30. Comparison of accelerated and non-accelerated capacity loss versus number of cycles.

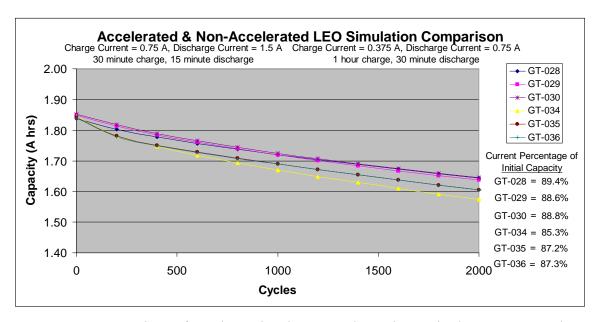


Figure 31. Comparison of accelerated and non-accelerated capacity loss versus number of cycles.

Figures 28 and 30 compare the accelerated and non-accelerated cells on the same graph, using the scale of the 4000 cycles the accelerated testing has completed. Figures 29 and 31 compare the same data, except anything after the 2000th cycle on the accelerated test has been truncated. Looking at these two graphs, and the corresponding

current percentage of initial capacity, it is apparent that the accelerated testing is not accurately predicting the non-accelerated testing results. As seen in earlier chapters, a direct correlation has been seen in the amount of capacity loss as compared to the charge/discharge rate. This could be the reason for the difference in the capacity loss between the two tests. For both charge rates, the cells going through the accelerated test are one to two percentage points less than the non-accelerated test at the same point. If the accelerated testing was a good representation of the non-accelerated testing, both the cells going through the accelerated and non-accelerated testing would have the same percentage of initial capacity at the same cycle. Therefore, the above procedures conclude that the accelerated testing is not a good representation of how cells will lose capacity under real time conditions.

The next step was to compare capacity loss over total test time to see if there was any correlation. Graphs of these test results are shown in Figures 32 and 33.

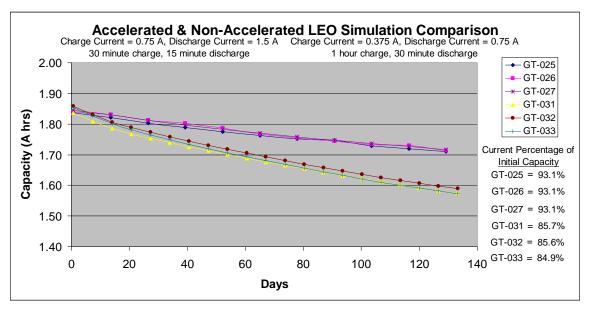


Figure 32. Comparison of accelerated and non-accelerated capacity loss versus number of days.

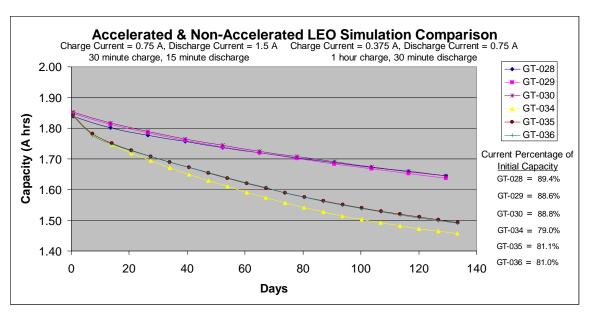


Figure 33. Comparison of accelerated and non-accelerated capacity loss versus number of days.

Based on the results seen above, there is no correlation between the capacity loss over the total number of test days. As seen, the cells which are being cycled at the higher rate are losing capacity at a higher rate than the cells being cycled at the lower rate. This agrees with results seen earlier, and has no impact on the accelerated testing. Additionally, when comparing based on the total number of days, the accelerated testing has completed twice as many cycles as the non-accelerated.

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X. CONCLUSION / RECOMMENDATIONS

A. CONCLUSION

Overall, all aspects of the characterization of graphite lithium-ion cells were positive. The cells suffered no negative effects while undergoing vibrations similar to those experienced during a spacecraft launch. With the cell capacity slightly increasing during vibration testing, it could be that the launch environment could be a positive effect on the cells, although more research would be required on this subject.

As the cells were cycled at various temperatures, the graphite cells continued to provide very flat discharge curves throughout the temperature range. The graphite cells far outperformed the hard carbon cells by providing a much flatter discharge profile over a variety of temperatures.

It was determined that cell voltage drift is not a factor that needs to be included when matching cells for a battery. The reason behind this is that the voltage drift seen in the graphite cells was minimal. With less than a 2 mVolt difference at the highest charge rate tested, the drift is not an issue.

While not analyzed on graphite cells, the capacity loss in storage for the hard carbon cells provided good results. After over 18 months in storage at 0°C, the cells lost an average capacity of less than 2%. With the graphite cells far outperforming the hard carbon cells in all other aspects of this research, it is assumed that the graphite cells will equal or surpass the storage time of the hard carbon cells.

The LEO and accelerated LEO simulations have, so far, provided good data on how graphite cells would perform on orbit. This testing should continue for months to years to see how long these cells will last as they are cycled. Additionally, data from the accelerated testing should continue to be gathered to provide input as to the validity of accelerated testing.

Finally, the research completed on graphite lithium-ion cells strongly supports the opinion that they are far superior to hard carbon. With the flat discharge curve, excellent

temperature tolerance, and durability in the launch environment, the graphite cell would make a great cell to comprise a spacecraft battery.

B. RECOMMENDATIONS

The first recommendation is that the LEO and accelerated LEO tests that are currently running should be continued. The results listed in this thesis are based on almost five months of data. To get an accurate representation of how the cells perform over years of cycling, these tests need to keep running. Additionally, the continuation of the accelerated LEO testing will help to determine if it is or is not an accurate representation of how cells will lose capacity under real time conditions.

For all follow-on work on graphite lithium-ion cells, it is recommended that the cells be cycled 10 times before an initial capacity check is performed. This is due to the observation that the graphite cells appear to gain some capacity over the first few cycles. The initial 10 cycles will allow the cell to get over the initial capacity gain and all procedures will be correlated better.

A very interesting and needed test is capacity loss versus time while a cell is in storage. This would be very important to the timing of the building of a battery for Naval Postgraduate School's student built satellite, NPSAT1. This should include cells stored at different temperatures and different Depths of Discharge (DOD). Store one set in the refrigerator and another set at a temperature of around 20° to 25° C. If it is possible, storage at other temperatures should also be performed. Additionally, at each temperature, store cells at 0%, 50% and 75% DOD. Results from these tests will determine the optimal temperature to store lithium-ion cells. The procedure for this test should be an initial capacity check, and then a capacity check every three to six months for an extended period of time. Additionally, some cells should be initially cycled 40 to 50 full cycles to determine the capacity loss versus number of cycles. This result can then be subtracted from the calendar life tests to determine the true capacity loss while in storage.

Another needed test is to determine if the capacity increase seen in the random vibration testing is permanent or temporary. This should be accomplished through the

use of two separate groups of cells. One group of cells should go through the identical vibration testing procedures listed in this thesis. The second group of cells should go through the same vibration testing procedures, except for the actual vibration portion. This will ensure that all cells have the same amount of cycles at the conclusion of the vibration procedures. At this point, all cells should be run through a LEO simulation procedure for months to years, comparing the vibrated and non-vibrated cells to determine if the capacity increase is long term.

APPENDIX A (DISASSEMBLY PROCEDURES FOR SONY BP-GL95 LITHIUM ION BATTERY PACKS)

The following steps are used for dismantling the Sony BP-GL95 Lithium Ion Battery Pack as shown below. The battery pack itself contains twelve Sony US18650 Graphite Lithium-Ion Cells.



Figure 34. Sony BP-GL95 lithium ion battery pack.

After obtaining the battery pack, flip it over so that the label is facing the working surface. Six torx tamper resistant screw heads will be seen in recessed holes. These can be removed with a size TT7 screw bit. After all the screws have been removed, the side of the battery case that is facing up can be removed. It may take a little bit of effort, but the six screws that were removed are all that holds the two pieces of the case together. The result is pictured below.



Figure 35. Sony BP-GL95 with cover removed.

The next step is to remove all the solder tabs that connect the circuit board to the individual cells. These can either be cut or desoldered. Additionally, there is a set of black wires sticking up through the circuit board; this needs to be cut. Once the circuit board is removed, the ten cells that are laid out parallel to each other can be removed as one group as pictured below.



Figure 36. Graphite cells removed from Sony BP-GL95 battery pack.

After removing the ten cells, use a flat tipped screwdriver to pry off the plastic cover that is covering the remaining two cells as pictured below.

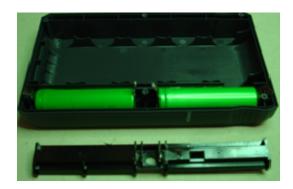


Figure 37. Final two cells in Sony BP-GL95 battery pack.

These two cells can then be lifted out of the battery case. Next, use needle nose pliers and remove all solder tabs that are connected to the cells and any glue or tape on the sides of the cells. Be careful as the ends of the cells will have sharp metal where the solder tabs were connected.

After all cells have been separated and everything removed, use a Dremel Multipro with a grinding bit installed to carefully grind down the ends of the cells. The idea is to grind off the remnants of the solder tabs without grinding off too much of the cell material. When the ends are smooth to the touch, the cell is ready for use.

APPENDIX B (DESCRIPTION OF MACCOR BATTERY TEST SYSTEM)

The MACCOR battery test system in the Naval Postgraduate School battery lab consists of the following components. A MACCOR 2200 battery test system, a MACCOR 2300 battery test system, cooling plates encased in Plexiglas cases where the individual cells are placed for testing, a Dell computer that is a dedicated controller for the two test systems, a Dell computer that is a file server, and a Polyscience recirculator that is used to maintain temperature control for the testing cells.



Figure 38. MACCOR battery test system.

The MACCOR 2200 and MACCOR 2300 each consist of eight test channels, for a total capacity of sixteen separate testing channels. Each channel consists of four wires with alligator clips on the ends and a thermocouple. The wires consist of two black and two red wires. For each color, there is one thin and one thick wire. The thick wires provide the charge or discharge current for the individual channel, while the thin wires

provide the input for the collected data. The thermocouple provides an accurate temperature for the individual channel. The MACCOR 2200 is connected via an Ethernet cable to the MACCOR 2300, and it is in turn connected to the controller computer.

The controller computer runs Microsoft 98 as an operating system, and has all the software installed to control the battery test systems. This computer is not on the school network. It is on a private network that includes only the controller and the server computers. It is important that no other software is loaded on the controller computer as it will cause the system to slow down and eventually crash, resulting in the temporary interruption of any tests in progress. All test data is stored on the controller computer. currently in in Tests that are progress are stored the folder C:/Maccor/System/Navalpst/active. Tests that have completed and been cleared from the channel they were being performed on are stored in the folder C:/ Maccor/System/Navalpst /archive.

The server computer runs Microsoft XP as an operating system, and has the MACCOR server software installed on it. This computer is on the school network and is accessible remotely. The server is connected to the controller through an Ethernet connection. The server polls the controller every two hours and copies all data from the active and archive directories and stores it on the server. The idea behind the server is that it can poll multiple MACCOR controllers and store all the data in one central area. All data can be found in the following directory the on server: C:/Data/MIMS/Indexed/ASCIIfiles/NAVALPST.

Operating manuals for all the MACCOR battery test systems and software can be found in a binder in the battery lab, or in the file "V2_5 manual 7 2002" located on the desktop of the server. As of this thesis, the current version of the manual is extremely outdated. MACCOR support is working on an update and will post it once it is complete. As the operating manual and controller software is updated, MACCOR will post the updates on their website www.maccorsw.com. The login and password for the current update can be obtained by contacting MACCOR customer support at (918) 446-1874.

APPENDIX C (CALIBRATION PROCEDURES FOR MACCOR BATTERY TEST SYSTEM)

Objectives

To calibrate the MACCOR 2200 and MACCOR 2300 battery test systems.

General information on calibration

There are two parts to the calibration of the MACCOR battery test systems. First is the calibration of the current and voltage on the systems, second is the calibration of the thermocouples. You will need to have plenty of time available for the calibration as this process requires approximately 30 minutes for setup and 10 minutes for each channel. The thermocouple calibration will take around 10 minutes to do all 16 channels. The entire process will take around 3 ½ hours.

Equipment required for calibration of battery test system

This calibration requires the following equipment for the battery test system calibration: the MACCOR battery test systems and attached computer system; an Agilent 34401A Multimeter; a MACCOR designed serial cable to attach 34401A to the computer serial port; three cells with a charge of approximately 2.5V each, with solder tabs; and five banana clip cables. For the thermocouple calibration you will need an Omega Model CL24 Calibrator – Thermometer, and a T-type thermocouple cable.

Set-up

Turn on all MACCOR systems and start the MACCOR32.exe program. You need to verify that all 16 channels are available, as indicated by the black letters "Available" with a white background, and there are no error messages in the "System status" area. Once verified that all channels are operational, shut down MACCOR32.exe by clicking on "File" and selecting "Shutdown and Exit". Then open up the MACCOR calibration software, MaccorCal.exe. Click on the "Calibrate" tab. On the right side of

the window, you will see the title "Options". Under "Type", select "Current & Voltage". Under "Input", select "Automatic". Under "Tasks", select "Calibrate-Verify". Under "Mode", check both "Charge" and "Discharge". Under "Ranges", check all four blocks for "Range 1" through "Range 4". Under "Channels", select "Single Channel".

Plug the serial cable into the 34401A and serial port 1 of the MACCOR computer. A pinout of the cable is pictured at the end of this appendix in Figure 45.

Power the Agilent 34401A. Once powered up, push the "shift" button, followed by the "<" button to access the menu. Press the ">" key until the screen reads "E: I/O MENU", then press the "v" key once.

The screen will say "1: GPIB ADDR", press the "v" key once. The screen should say "22 ADDR", if not, press the ">" key to highlight the first number, then use the "v" or "^" keys to change it to "2", then do the same with the second number. Then press the "<" key twice so the numbers are not highlighted and press the "^" key once to get back to the screen that says "1: GPIB ADDR", then press the ">" button.

The screen will say "2: INTERFACE". Press the "v" button and the screen should read "RS-232". If not, use the "<" and ">" buttons to set it to "RS-232". Press the "^" button to get back to the screen that says "2: INTERFACE". Then press the ">" button.

The screen will read "3: BAUD RATE". Press the "v" button and the screen should read "9600 BAUD". If not, use the "<" and ">" buttons to set it to "9600 BAUD". Press the "^" button to get back to the screen that reads "3: BAUD RATE". Then press the ">" button.

The screen will read "4: PARITY". Press the "v" button and the screen should read "NONE: 8 BITS". If not, use the "<" and ">" buttons to set it to "NONE: 8 BITS". Press the "^" button to get back to the screen that reads "4: PARITY". Then press the ">" button.

The screen will read "5: LANGUAGE". Press the "v" button and the screen should read "SCPI". If not, use the "<" and ">" buttons to set it to "SCPI". Press the "Auto/Man" button. This will save any changes you made and will bring you to the main screen.

Place three 2.5V cells in series with alligator clips holding the tabs together. Secure these cells in a way so the cells do not short. The cells do not have to be exactly at 2.5V; the only requirement is that the combined voltage of the three cells cannot exceed 10V. If 10V is exceeded, it will not damage anything; however the MACCOR software will stop the calibration process due to over voltage.

Plug one banana clip cable into the top right Input (HI) of the AGILENT 34401A and hook it to the S+ cable (the thin red one) on the Channel 1 cable. Plug another banana clip cable into the middle right Input (LO) and hook both the S- and B- cables (the black ones) on the Channel 1 cable. Plug another banana clip cable into the lower right Input (I) and hook it to the B+ cable (the thick red one) on the Channel 1 cable. Then plug an additional banana plug cable into each of the top two inputs (HI and LO) and place them near the batteries, but not touching them or each other.

Set up is now complete.

Calibration of battery test system

The first part of the calibration process is calibrating the current; the second part is calibrating the voltage. With all cables correctly hooked up, press the "start" button on the bottom of the screen to start the calibration process. Look at the Agilent 34401A

screen. It will read "MACCOR" for a brief moment to let you know the connection to the computer is correct. It will then start showing current and voltage readings during the calibration process.

Press the "Activity" button on the lower left corner of the screen of the MACCOR calibration window, this will open up a window that will display calibration details as each portion of the channel is calibrated. If a step fails, it will retry the step again. If it fails again, it will move on to the next step. Monitor these as the calibration process proceeds. If the calibration process completes and there is still a portion that failed, you will need to rerun the calibration on that channel. Before you rerun it, read the section "What to do if calibration fails", located immediately before the thermocouple calibration section.

When current calibration is complete, the software moves on to the voltage calibration. The process is different for the 2200 and the 2300. Since Channels 1-8 are the 2300, those instructions are listed first. Throughout the process, you will be asked to provide voltages of -2.5V, 2.5V, 0V, 5V, and 7.5V. These are only approximate voltages and are not hard requirements. The cells themselves will provide voltages so that the testing equipment and software can build the calibration tables.

MACCOR 2300

You will receive a pop-up window asking for a -2.5V source. Connect cable for -2.5V and press the "OK" button. This is pictured in Figure 39.

Next you will receive a pop-up window asking for a 2.5V power source. Connect cable for 2.5V and press the "OK" button. This is pictured in Figure 40.

You will then receive a pop-up window asking for a 2.5V power source again. Since you are already connected for that, just press the "OK" button again.

You will then receive a pop-up window asking for 0V. Take the two banana clips connected to the alligator clips and hook them together without the battery and press the "OK" button. This is pictured in Figure 41.

Finally, you will receive a pop-up window asking for -2.5V again. Connect cable for -2.5V and press the "OK" button.

The next windows will indicate that calibration is complete and calibration settings have been saved. Just press "OK" on these and move on to step 4.

MACCOR 2200

You will receive a pop-up window asking for a 2.5V power source. Connect cable for 2.5V and press the "OK" button. This is pictured in Figure 40.

Next you will receive a pop-up window asking for a 7.5V power source. Connect cable for 7.5V and press the "OK" button. This is pictured in Figure 44.

You will then receive a pop-up window asking for a 7.5V power source again. Since you are already connected for that, just press the "OK" button again.

You will then receive a pop-up window asking for a 5V power source. Connect cable for 5V and press the "OK" button. This is pictured in Figure 43.

Finally, you will receive a pop-up window asking for 2.5V again. Connect cable for 2.5V and press the "OK" button.

The next windows will indicate that calibration is complete and calibration settings have been saved. Just press "OK" on these and move on to step 4.

When a channel has been successfully calibrated, hook the Agilent 34401A up to the next channel and repeat the steps until you have calibrated all channels.

Once all channels are calibrated, close the calibration software. If the software prompts you to save calibration values, check yes. This is a redundant operation as calibration settings are saved automatically after each channel is completed.

What to do if calibration fails on the battery system

If any portion of the calibration procedure fails, look at the percentage rate of failure. If it is less than 1 to 2 percent, just rerun the calibration process on that channel. The software makes small (incremental) changes each try, so it may take several attempts for a failed channel to pass the calibration. If the error percentage is high, first check all the connections and ensure they are hooked up correctly and securely. If all connections are correct, and you still get a large error, you most likely have some sort of hardware problem and will need to get in touch with MACCOR tech support.

<u>Calibration of the thermocouples</u>

Setup

First, disconnect all the thermocouples connected to the MACCOR test systems to be calibrated.

Next, turn on the CL24. You should see the letters "CALIB" on the screen. If not, you will see "METER", in which case you need to press the "CALIB/METER" button until "CALIB" appears. Look at the plug on the end of the thermocouples you just disconnected from the MACCOR battery test system. You will see a letter telling you which type of thermocouples they are. This type is based on the material the thermocouple is made of. For this system, it reads "T". You will see an indicator for thermocouple type at the top of the screen, this should read "T". If you see anything else, press the "SENSOR SELECT" button until it has changed to "T". Look in the lower right of the screen, you should see "OC". If it shows "OF", press the "OF/OC" button until "OC" is displayed.

Next you need to program calibration temperatures, and store them into memory locations in the CL24. This will make the calibration process much faster. First, press the "Change/Enter" button, the numerical display will start the flash. Press the number 1 one time to make the readout read 0.1. Then press the "Change/Enter" button again, the numerical display will stop flashing. Then press "Store" and "1". A number 1 will show up in the upper left corner of the screen. Then, press the "Change/Enter" button, the numerical display will start the flash. Press the number 5 one time, and the number 0 twice to make the readout read 50.0. Then press the "Change/Enter" button again, the numerical display will stop flashing. Then press "Store" and "2". A number 2 will show up in the upper left corner of the screen. At this point you have programmed two temperatures into the CL24.

Next you will need to plug the thermocouple calibration cable into port T1 of the CL24. Port one is the left port if you are looking at the screen. If you pull back the rubber housing, you will see the T1 and T2 labels. Plug the other end of the cable into the MACCOR 2300 in channel 1.

Calibrating the Thermocouples

Open up the MACCOR testing software. Go to the "Maintenance" menu and select "Setup and Maintenance". When the screen comes up, select "Config Auxiliary Inputs". You will be brought to a screen titled "Auxiliary Inputs". (The steps to follow from this point forward for the MACCOR 2200 and the MACCOR 2300 are identical except you need to keep in mind the MACCOR 2300 is "**Board 1**" and the MACCOR 2200 is "**Board 2**")

The following steps will take you through calibrating the MACCOR 2300 thermocouples in detail. First highlight "Ai **Board 1** Panel 1 Thermocple" and press "OK". Then click on "Board 1, Panel 1, Pos 01" and the entire row will turn blue. Then click on "Calibrate single" You will get a pop-up window asking to "set low reference" (this is the low temperature setting the system will use to build its calibration table).

On the CL24, press the "Recall" and "1" button, the display will read 0.1 °C. In the pop-up window, type in 0.1 and press "OK". The box will disappear for a second and come back up asking the "set high reference". Press the "Recall" and "2" button, the display will read 50 °C. In the pop-up window, type in 50 and press "OK" (this is the high temperature setting the system will use to build its calibration table). The window will disappear and you will see the "Offset" number change in that row. Unplug the thermocouple from channel 1 and plug it into channel 2.

Click on "Board 1, Panel 1, **Pos 02**" and repeat the above steps until all 8 channels are complete. Then, you will need to click on the "Exit" button to return to the "Maintenance" menu. Remove the thermocouple from channel 8 and plug it in channel 1 of the MACCOR 2200.

Next, click on the "Config Additional Inputs" again, and highlight "Ai **Board 2** Panel 1 Thermocple" and press "OK". You will come back to the same screen you had earlier. However, you will now need to scroll down until you find "Board 2, Panel 1, Pos 01" Then repeat the above steps until all 8 channels on the MACCOR 2200 are complete.

When the MACCOR 2200 is complete, press the "Exit" button to return to Maintenance View Screen. Then press "Return to Main Status" to get back to the main screen. Ensure all thermocouples are plugged back into their correct location. Each thermocouple plug is marked with its corresponding auxiliary input position.

This completes the complete calibration of the MACCOR Battery Test Systems.

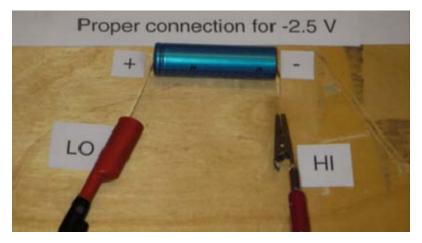


Figure 39. Proper connection for -2.5 V.

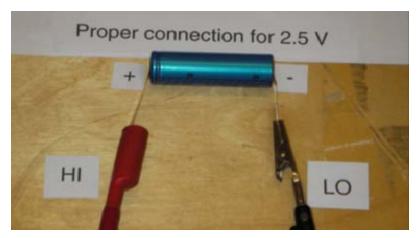


Figure 40. Proper connection for 2.5 V.



Figure 41. Proper connection for 0 V.

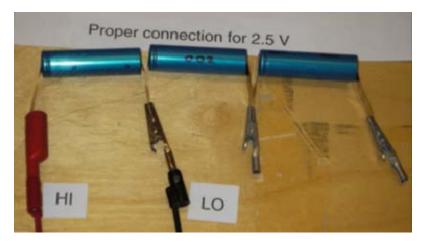


Figure 42. Proper connection for 2.5V.

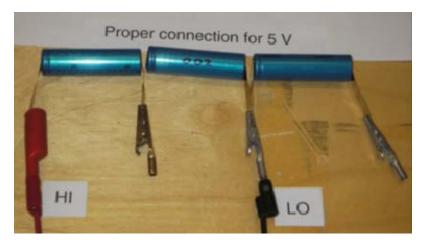


Figure 43. Proper connection for 5 V.

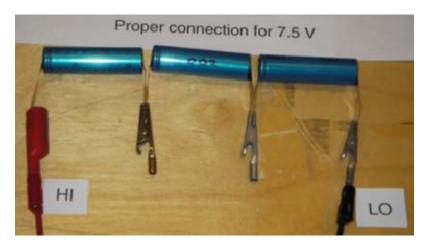


Figure 44. Proper connection for 7.5 V.

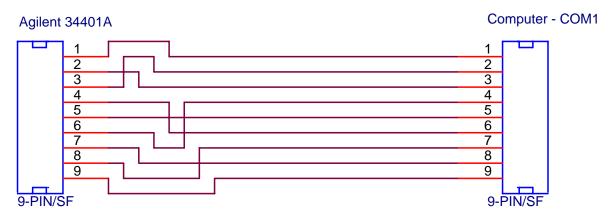


Figure 45. Pin-out of calibration cable.

APPENDIX D (DESCRIPTION OF THIN-LINE SERIES 80 PARALLEL GAP WELDER)

The Thin-Line Series 80 parallel gap welder consists of two components. The first is the Dual Pulse 125 Stored Energy Resistance Welding Power Supply, and the second is the Thin-Line model 88F parallel gap welder.

The Dual Pulse 125 is a stored energy, capacitor discharge, power supply designed to perform precision resistance welding. It has the ability to store up to eight different weld schedules, allowing for different energy levels for each side of a cell.[11]



Figure 46. Dual Pulse 125 Stored Energy Resistance Welding Power Supply.

The Thin-Line model 88F parallel gap welder is used to weld solder tabs onto the ends of the graphite lithium-ion cells. In this application, both electrodes of the welder contact the same solder tab. When the foot pedal is depressed, the electrodes lower to the solder tab and exert a pressure on the solder tab and end of the cell. The current then flows from one electrode, through the solder tab and end of the cell, and to the other electrode, resulting in the solder tab being welded to the end of the cell.[12]



Figure 47. Thin-Line Model 88F Parallel Gap Welder.

APPENDIX E (DESCRIPTION OF POLYSCIENCE RECIRCULATOR)

The Polyscience recirculator, Model 5205, is designed to circulate fluid through the thermal plates on the table, thus maintaining a constant temperature for the cells.[13]



Figure 48. Polyscience recirculator.

The recirculator contains Dynalene HC-30 as the recirculator fluid. Dynalene HC-30 is a water based heat transfer fluid designed for temperature ranges from -30° C to 218° C.[14] Using the controls on the front of the recirculator, the desired temperature can be set. The display window will show the current temperature of the fluid. It is important to note that the temperature on the recirculator may not match the temperature the thermocouples register at the individual cells. Once the recirculator has equalized the temperature, check the thermocouple temperature and make small adjustments to the recirculator as needed.

APPENDIX F (CONTROL TEST PROCEDURES)

Overview:

This procedure is the control for all short term testing done on the Graphite Lithium Ion Cells. Each cycle will charge the cells to 4.1 Volts and then discharge them to 3.0 Volts. The charge rate of each test is the same as the discharge rate. The rates used for these tests are 0.35 Amps and 0.70 Amps. Each test is set up to perform the cycle 20 times before ending the test. Each cycle is a measurement of the test cell's capacity, so no special provisions are made to perform a capacity measurement. At the conclusion of the 20 cycles, the cell will rest for 30 minutes with data being recorded every second to measure the drift of the cell once charging is complete. Below are listed the actual procedures as they are programmed into the MACCOR battery test system.

Purpose:

To identify normal capacity loss so it can be accounted for in other tests.

File "T-Cont-1" - Control at 0.35 A charge and discharge rate from 4.1 V to 3.0 V

Step	Type	Mode	Val	Limit	Val	End Type	Ор	Val	Goto	Rpt Type	Val	Option
1	Charge	Current	0.35	Voltage	4.1	Voltage	>=	4.1	002	StepTime	0:05:00	4NNN
2	AdvCycle											
3	Do 1											
4	Charge	Current	0.35	Voltage	4.1	Voltage	>=	4.1	005	StepTime	0:05:00	4NNN
5	Discharge	Current	0.35	Voltage	3.0	Voltage	<=	3.0	006	StepTime	0:05:00	4NNN
6	AdvCycle											
7	Loop1					Loop Cnt	=	20	800			
8	Charge	Current	0.35	Voltage	4.1	Voltage	>=	4.1	009	StepTime	0:05:00	4NNN
9	Rest					StepTime	=	0:30:00	010	StepTime	0:00:01	4NNN
10	End											

File "T-Cont-2" - Control at 0.70 A charge and discharge rate from 4.1 V to 3.0 V

Step	Type	Mode	Val	Limit	Val	End Type	Ор	Val	Goto	Rpt Type	Val	Option
1	Charge	Current	0.70	Voltage	4.1	Voltage	>=	4.1	002	StepTime	0:05:00	4NNN
2	AdvCycle											
3	Do 1											
4	Charge	Current	0.70	Voltage	4.1	Voltage	>=	4.1	005	StepTime	0:05:00	4NNN
5	Discharge	Current	0.70	Voltage	3.0	Voltage	>=	3.0	006	StepTime	0:05:00	4NNN
6	AdvCycle											

7	Loop1					Loop Cnt	Ш	20	800			
8	Charge	Current	0.70	Voltage	4.1	Voltage	, ,	4.1	009	StepTime	0:05:00	4NNN
9	Rest					StepTime	=	0:30:00	010	StepTime	0:00:01	4NNN
10	End											

APPENDIX G (RANDOM VIBRATION TESTING PROCEDURES)

Overview

This test subjects cells to a random vibration test with a spectrum equal to the launch environment to measure capacity loss from vibration. The procedure will consist of two groups of three cells, which will be run through two full charge/discharge cycles (4.1 Volts to 3.0 Volts), with a capacity measurement being performed on the second discharge cycle. Each group will have a different current; the rates will be 0.35 Amps and 0.70 Amps. The temperature will be kept constant at 25° C. The cells will then undergo random vibration testing on all three axes, with a capacity measurement being performed after each axis. The capacities will then be compared to see if there is any capacity loss due to the launch environment using data from the control group.

Procedures:

Initial Break-in/Capacity Check:

This procedure charges the cells to 4.1 Volts and then discharges them to 3.0 Volts. The cycle is repeated twice with a capacity check being performed on the second cycle. At the completion of the second cycle, prior to vibration testing, the cell is charged back up to 4.1 Volts for the vibration test. The charge rate of each test is the same as the discharge rate. The rates used for these tests are 0.35 Amps and 0.70 Amps.

File "T-VibB-1" – Vibration Testing for 0.35 A charge and discharge rate

Step	Туре	Mode	Val	Limit	Val	End Type	Ор	Val	Goto	Rpt Type	Val	Option
1	Charge	Current	0.35	Voltage	4.1	Voltage	>=	4.1	002	StepTime	0:05:00	4NNN
2	AdvCycle											
3	Do 1											
4	Charge	Current	0.35	Voltage	4.1	Voltage	>=	4.1	005	StepTime	0:05:00	4NNN
5	Discharge	Current	0.35	Voltage	3.0	Voltage	<=	3.0	006	StepTime	0:05:00	4NNN
6	AdvCycle											
7	Loop1					Loop Cnt	=	2	800			
8	End											

File "T-VibB-2" – Vibration Testing for 0.70 A charge and discharge rate

Step	Туре	Mode	Val	Limit	Val	End Type	Ор	Val	Goto	Rpt Type	Val	Option
1	Charge	Current	0.70	Voltage	4.1	Voltage	 	4.1	002	StepTime	0:05:00	4NNN
2	AdvCycle											
3	Do 1											
4	Charge	Current	0.70	Voltage	4.1	Voltage	>	4.1	005	StepTime	0:05:00	4NNN
5	Discharge	Current	0.70	Voltage	3.0	Voltage	<=	3.0	006	StepTime	0:05:00	4NNN
6	AdvCycle											
7	Loop1					Loop Cnt	=	2	800			
8	End											

Post Vibration Capacity Check:

This procedure charges the cells to 4.1 Volts and then discharges them to 3.0 Volts to measure capacity. At the completion of the cycle, prior to vibration testing, the cell is charged back up to 4.1 Volts for the vibration test. The charge rate of each test is the same as the discharge rate. The rates used for these tests are 0.35 Amps and 0.70 Amps.

File "T-Vib-1" – Vibration Testing for 0.35 A charge and discharge rate

Step	Type	Mode	Val	Limit	Val	End Type	Ор	Val	Goto	Rpt Type	Val	Option
1	Charge	Current	0.35	Voltage	4.1	Voltage	<u>۷</u>	4.1	002	StepTime	0:05:00	4NNN
2	Discharge	Current	0.35	Voltage	3.0	Voltage	=	3.0	003	StepTime	0:05:00	4NNN
3	Charge	Current	0.35	Voltage	4.1	Voltage	> =	4.1	004	StepTime	0:05:00	4NNN
4	End											

File "T-Vib-2" – Vibration Testing for 0.70 A charge and discharge rate

Step	Туре	Mode	Val	Limit	Val	End Type	Ор	Val	Goto	Rpt Type	Val	Option
1	Charge	Current	0.70	Voltage	4.1	Voltage	\ 	4.1	002	StepTime	0:05:00	4NNN
2	Discharge	Current	0.70	Voltage	3.0	Voltage	"	3.0	003	StepTime	0:05:00	4NNN
3	Charge	Current	0.70	Voltage	4.1	Voltage	>=	4.1	004	StepTime	0:05:00	4NNN
4	End											·

Vibration Testing:

Calibrate accelerometers:

- 1. Place accelerometer on tip of Calibrated Exciter using vibration wax.
- 2. Attach other end of accelerometer to Channel 1 of Agilent 35670A Dynamic Signal Analyzer.
- 3. Power on the Agilent 35670A.
- 4. Press the save/recall button.
- 5. Press F8 to turn on the catalog.
- 6. Using the dial highlight "ACC-CAL.STA"
- 7. Press F5 for "Recall State"
- 8. Press F1 for "Enter" to select the program.
- 9. Press F8 to turn off the catalog.
- 10. Turn on the Calibrated Exciter.
- 11. Press Start on the Agilent 35670A.
- 12. When "Average Complete" shows record the X and Y values.

Calculation for Y (sensitivity) value.

- This value is in the units of mVrms, which is the same as $\frac{m v}{10 \frac{m}{s^2}}$
- Use the following equation to convert to mV/g, which is the program format.
- "Y value" / 10 * 9.80665 = mV/g

Assemble all six cells in clamp

Weigh the complete assembly with the bolts used to attach it to the vibration table. Ensure the weight is obtained in pounds.

Set up vibration software:

- 1. Power on computer and let boot up.
- 2. Select VibEdit.
- 3. Set up vibration software for test.
- 4. Enter in Sensitivity as per above calculations.
- 5. Enter in weight of assembly.
- 6. Save and close VibEdit.

Run vibration test

- 1. Open VibRunner.
- 2. Open file saved from above.
- 3. Perform a Self Test.
- 4. When Self Test passes, click on Run.

APPENDIX H (FAMILY OF CURVES PROCEDURES)

Overview

This test consists of gathering data to build a family of curves that will specify an expected graph of capacity versus temperature for these cells. The procedure consists of two groups of three cells, which will be run through a break in procedure of one full charge/discharge cycle to get an initial capacity measurement. The cells will then go through procedures where they are discharged at constant current from 4.1 Volts down to 3.0 Volts. This procedure will be repeated every five degrees from 5° C to 40° C. This test will be repeated at currents of 0.35 Amps and 0.70 Amps. These two currents were chosen because a previous thesis was done that provided a family of curves for hard carbon lithium-ion cells,[3] and by using the same currents, the family of curves can be compared. The results will then be graphed as a family of curves.

Step 1: Initial Break-in:

This procedure charges the cells to 4.1 Volts and then discharges them to 3.0 Volts as an initial break-in of the cells. The charge rate of each test is the same as the discharge rate. The rates used for these tests are 0.35 Amps and 0.70 Amps. The temperature will be kept at 5° C.

File "T-FOCB-1" – Family of Curves break-in for 0.35 A charge and discharge rate

Step	Туре	Mode	Val	Limit	Val	End Type	Ор	Val	Goto	Rpt Type	Val	Option
1	Charge	Current	0.35	Voltage	4.1	Voltage	II A	4.1	002	StepTime	0:05:00	ANNN
2	Discharge	Current	0.35	Voltage	3.0	Voltage	v =	3.0	003	StepTime	0:05:00	ANNN
3	End											

File "T-FOCB-2" – Family of Curves break-in for 0.70 A charge and discharge rate

Step	Туре	Mode	Val	Limit	Val	End Type	Ор	Val	Goto	Rpt Type	Val	Option
1	Charge	Current	0.70	Voltage	4.1	Voltage	\ \	4.1	002	StepTime	0:05:00	ANNN
2	Discharge	Current	0.70	Voltage	3.0	Voltage	٨	3.0	003	StepTime	0:05:00	ANNN
3	End											

Step 2: Family of Curves Procedure:

This procedure charges the cells to 4.1 Volts, rests for 10 minutes to allow the cells to drift to a stable starting point, and then discharges them to 3.0 Volts. The cycle is performed at 5° C increments from 5° C to 40° C. The charge rate of each test is the same as the discharge rate. The rates used for these tests are 0.35 Amps and 0.70 Amps.

File "T-FOC-1" – Family of Curves for 0.35 A charge and discharge rate

Step	Type	Mode	Val	Limit	Val	End Type	Ор	Val	Goto	Rpt Type	Val	Option
1	Charge	Current	0.35	Voltage	4.0	Voltage	ļļ A	4.0	002	StepTime	0:05:00	ANNN
2	Rest					StepTime	II	0:10:00	003	StepTime	0:00:01	ANNN
3	Discharge	Current	0.35	Voltage	3.0	Voltage	\=	3.0	004	StepTime	0:00:01	ANNN
4	End											

File "T-FOC-2" - Family of Curves for 0.70 A charge and discharge rate

Step	Type	Mode	Val	Limit	Val	End Type	Ор	Val	Goto	Rpt Type	Val	Option
1	Charge	Current	0.70	Voltage	4.0	Voltage	>=	4.0	002	StepTime	0:05:00	ANNN
2	Rest					StepTime	=	0:10:00	003	StepTime	0:00:01	ANNN
3	Discharge	Current	0.70	Voltage	3.0	Voltage	<=	3.0	004	StepTime	0:00:01	ANNN
4	End											

APPENDIX I (VOLTAGE DRIFT PROCEDURES)

Overview:

This test consists of gathering data to determine the amount of voltage drift a cell experiences upon completion of a charge or discharge cycle. Each cycle will charge the cells to 4.1 Volts and allow them to rest for 30 minutes. At the completion of this rest period, the cell will be discharged to 3.0 Volts and allowed to rest for 30 minutes. The charge rate of each test is the same as the discharge rate. The rates used for these tests are 0.35 Amps and 0.70 Amps. Below are listed the actual procedures as they are programmed into the MACCOR battery test system.

Purpose:

To identify voltage drift at the completion of a charge and discharge cycle.

File "T-Rest-1" – Drift at 0.35 A rate from 4.1 V to 3.0 V

Step	Type	Mode	Val	Limit	Val	End Type	Ор	Val	Goto	Rpt Type	Val	Option
1	Charge	Current	0.35	Voltage	4.1	Voltage	 	4.1	002	StepTime	0:01:00	4NNN
2	Rest					StepTime	II	0:30:00	003	StepTime	0:00:01	4NNN
3	Discharge	Current	0.35	Voltage	3.0	Voltage	۱	3.0	004	StepTime	0:01:00	4NNN
4	Rest					StepTime	II	0:30:00	005	StepTime	0:00:01	4NNN
5	Charge	Current	0.35	Voltage	4.1	Voltage	II A	3.8	006	StepTime	0:01:00	4NNN
6	End											

File "T-Rest-2" – Drift at 0.70 A rate from 4.1 V to 3.0 V

Step	Type	Mode	Val	Limit	Val	End Type	Ор	Val	Goto	Rpt Type	Val	Option
1	Charge	Current	0.70	Voltage	4.1	Voltage	 	4.1	002	StepTime	0:01:00	4NNN
2	Rest					StepTime	II	0:30:00	003	StepTime	0:00:01	4NNN
3	Discharge	Current	0.70	Voltage	3.0	Voltage	\=	3.0	004	StepTime	0:01:00	4NNN
4	Rest					StepTime	II	0:30:00	005	StepTime	0:00:01	4NNN
5	Charge	Current	0.70	Voltage	4.1	Voltage	>=	3.8	006	StepTime	0:01:00	4NNN
6	End	·										

APPENDIX J (CAPACITY LOSS IN STORAGE)

Overview:

This test consists of gathering data to determine the amount of capacity loss while in storage. Each cycle will charge the cells to 4.2 V and then discharge them to 2.5 V to obtain a capacity measurement. Over time, these capacity measurements will be graphed together to determine the loss while in storage. The charge rate of each test is the same as the discharge rate. The rates used for this test is 0.375 Amps. Below are listed the actual procedures as they are programmed into the MACCOR battery test system.

Purpose:

To identify capacity loss while in storage.

File "T-Life-1" - Drift at 0.35 A rate from 4.1 V to 3.0 V

Step	Туре	Mode	Val	Limit	Val	End Type	Ор	Val	Goto	Rpt Type	Val	Option
1	Charge	Current	0.375	Voltage	4.2	Voltage	ļ!	4.2	002	StepTime	0:05:00	4NNN
2	Rest					StepTime	11	0:01:00	003	StepTime	0:00:01	4NNN
3	Discharge	Current	0.375	Voltage	2.5	Voltage	۳	2.5	004	StepTime	0:05:00	4NNN
4	Rest					StepTime	1	0:01:00	005	StepTime	0:00:01	4NNN
5	Charge	Current	0.375	Voltage	4.2	Voltage	\ 	3.855	006	StepTime	0:05:00	4NNN
6	End											

APPENDIX K (LEO ACCELERATED AND NON-ACCELERATED TESTING PROCEDURES)

General info for all tests

The first step on all of these testing procedures is a one cycle break-in followed by an initial capacity check. This is a procedure that measures initial capacity of the individual cell. The maximum end of charge voltage (EOCV) allowed for any cell is 4.1 Volts. The minimum end of discharge voltage (EODV) allowed for any is 3.0 Volts. The limit of 4.1 Volts is used based on previous experiments showing a slightly slower loss of capacity with an EOCV of 4.1 Volts versus an EOCV of 4.2 Volts. The limit 3.0 Volts is for safety and limits for the lithium-ion battery technology. The temperature will be maintained at 25° C. The tables listed below are actual representations of MACCOR procedures as seen in the MACCOR software – "Build Procedure." All files are stored in the following directory on the computer hooked up to the MACCOR battery tester: C:\Maccor\procedur.

Test 1: (Capacity loss vs. cycles at various charge/discharge rates) LEO

This test cycles the cells on a 60-minute charge, 30-minute discharge cycle. This test simulates a LEO orbit, which is 60 minutes sunlight and 30 minutes eclipse. The discharge rate of each test is twice the charge rate. The charge rates used for these tests are 0.25 Amps and 0.375 Amps, which were chosen based on expected rates on orbit. If a voltage of 4.1 Volts is obtained prior to the 60-minute charge timeframe, the cell will go into a rest state for the remainder of the 60 minutes. This is to avoid trickle charging and simulate how the spacecraft would operate on orbit. After every 199th cycle of the initial test, the cell is charged to 4.1 Volts and then discharged to 3.0 Volts to provide a capacity measurement, and then charged back to 4.1 Volts to provide a uniform condition for the test. A current of 0.375 Amps was chosen for all tests on this capacitance measurement to provide a common baseline for all capacity tests. Each test is set up to perform the cycle 1000 times before ending the test.

File "T-LEO-1" - Capacity loss vs. cycles at 0.25 A charge, 0.5 A discharge rate

	rile i-	LEO-1	- Capa	icity 1055	V5.	cycles at c	1.25	A Charge	, 0.5	A discharg	je rate	
Step	Туре	Mode	Val	Limit	Val	End Type	Op	Val	Goto	Rpt Type	Val	Option
1	Do 1											
2	Charge	Current	0.375	Voltage	4.1	Voltage	>=	4.1	003	StepTime	0:05:00	4NNN
3	Discharge	Current	0.375	Voltage	3.0	Voltage	"	3.0	004	StepTime	0:05:00	4NNN
4	Loop 1					Loop Cnt	=	2	005			
5	Charge	Current	0.375	Voltage	4.1	Voltage	\	4.1	006	StepTime	0:05:00	4NNN
6	AdvCycle											
7	Do 3											
8	Do 2											
9	Charge	Current	0.250	Voltage	4.1	Voltage	 	4.1	010	StepTime	0:05:00	4NNN
						StepTime	Ш	1:00:00	011	StepTime	0:05:00	
10	Rest					StepTime	Ш	1:00:00	011	StepTime	0:05:00	4YNN
11	Discharge	Current	0.500	Voltage	3.0	Voltage	۱	3.0	012	StepTime	0:05:00	4NNN
						StepTime	=	0:30:00	013	StepTime	0:05:00	
12	Rest					StepTime	Ш	0:30:00	013	StepTime	0:05:00	4YNN
13	AdvCycle											
14	Loop 2					Loop Cnt	II	199	015			
15	Charge	Current	0.375	Voltage	4.1	Voltage		4.1	016	StepTime	0:05:00	4NNN
16	Discharge	Current	0.375	Voltage	3.0	Voltage	۳	3.0	017	StepTime	0:05:00	4NNN
17	Charge	Current	0.375	Voltage	4.1	Voltage	 	4.1	018	StepTime	0:05:00	4NNN
18	AdvCycle					-				-		
19	Loop 3					Loop Cnt	II	1000	020			
20	End											

File "T-LEO-2" - Capacity loss vs. cycles at 0.375 A charge, 0.75 A discharge rate

		ı	•			y 0103 at 0.					_	
Step	Туре	Mode	Val	Limit	Val	End Type	Op	Val	Goto	Rpt Type	Val	Option
1	Do 1											
2	Charge	Current	0.375	Voltage	4.1	Voltage	>=	4.1	003	StepTime	0:05:00	4NNN
3	Discharge	Current	0.375	Voltage	3.0	Voltage	<=	3.0	004	StepTime	0:05:00	4NNN
4	Loop 1					Loop Cnt	=	2	005			
5	Charge	Current	0.375	Voltage	4.1	Voltage	>=	4.1	006	StepTime	0:05:00	4NNN
6	AdvCycle											
7	Do 3											
8	Do 2											
9	Charge	Current	0.375	Voltage	4.1	Voltage	>=	4.1	010	StepTime	0:05:00	4NNN
						StepTime	=	1:00:00	011	StepTime	0:05:00	
10	Rest					StepTime	=	1:00:00	011	StepTime	0:05:00	4YNN
11	Discharge	Current	0.750	Voltage	3.0	Voltage	<=	3.0	012	StepTime	0:05:00	4NNN
						StepTime	=	0:30:00	013	StepTime	0:05:00	
12	Rest					StepTime	=	0:30:00	013	StepTime	0:05:00	4YNN
13	AdvCycle											
14	Loop 2					Loop Cnt	=	199	015			
15	Charge	Current	0.375	Voltage	4.1	Voltage	>=	4.1	016	StepTime	0:05:00	4NNN
16	Discharge	Current	0.375	Voltage	3.0	Voltage	<=	3.0	017	StepTime	0:05:00	4NNN
17	Charge	Current	0.375	Voltage	4.1	Voltage	>=	4.1	018	StepTime	0:05:00	4NNN
18	AdvCycle											
19	Loop 3					Loop Cnt	=	1000	020			
20	End											

Test 2: (Accelerated capacity loss vs. cycles at various charge/discharge rates) LEO

This is a test using an accelerated procedure to simulate a LEO orbit, which is 60 minutes sunlight and 30 minutes eclipse. The discharge rate of each test is twice the charge rate. The acceleration process doubles the current used, and halves the discharge and charge time. These procedures will be used to validate the acceleration process by accelerating tests T-LEO-1 and T-LEO-2 in Test 1. The charge rates used for these tests are 0.5 Amps and 0.75 Amps. After every 199th cycle of the initial test, the cell is charged to 4.1 Volts and then discharged to 3.0 Volts to provide a capacity measurement, and then charged back to 4.1 Volts to provide a uniform condition for the test. A current of 0.375 Amps was chosen for all tests on this capacitance measurement to provide a common baseline for all capacity tests. Each test is set up to perform the cycle 1000 times before ending the test.

File "T-ALEO-1" - Capacity loss vs. cycles at 0.5 A charge, 1 A discharge rate

Step	Type	Mode	Val	Limit	Val	End Type	Ор	Val	Goto	Rpt Type	Val	Option
1	Do 1											
2	Charge	Current	0.375	Voltage	4.1	Voltage	>=	4.1	003	StepTime	0:05:00	4NNN
3	Discharge	Current	0.375	Voltage	3.0	Voltage	<=	3.0	004	StepTime	0:05:00	4NNN
4	Loop 1					Loop Cnt	=	2	005			
5	Charge	Current	0.375	Voltage	4.1	Voltage	>=	4.1	006	StepTime	0:05:00	4NNN
6	AdvCycle											
7	Do 3											
8	Do 2											
9	Charge	Current	0.500	Voltage	4.1	Voltage	>=	4.1	010	StepTime	0:05:00	4NNN
						StepTime	=	0:30:00	011	StepTime	0:05:00	
10	Rest					StepTime	=	0:30:00	011	StepTime	0:05:00	4YNN
11	Discharge	Current	1.000	Voltage	3.0	Voltage	<=	3.0	012	StepTime	0:05:00	4NNN
						StepTime	=	0:15:00	013	StepTime	0:05:00	
12	Rest					StepTime	=	0:15:00	013	StepTime	0:05:00	4YNN
13	AdvCycle											
14	Loop 2					Loop Cnt	=	199	015			
15	Charge	Current	0.375	Voltage	4.1	Voltage	>=	4.1	016	StepTime	0:05:00	4NNN
16	Discharge	Current	0.375	Voltage	3.0	Voltage	<=	3.0	017	StepTime	0:05:00	4NNN
17	Charge	Current	0.375	Voltage	4.1	Voltage	>=	4.1	018	StepTime	0:05:00	4NNN
18	AdvCycle											
19	Loop 3					Loop Cnt	=	1000	020			
20	End											

File "T-ALEO-2" - Capacity loss vs. cycles at 0.75 A charge, 1.5 A discharge rate

_		ILLO Z								A discriai		
Step	Type	Mode	Val	Limit	Val	End Type	Op	Val	Goto	Rpt Type	Val	Option
1	Do 1											
2	Charge	Current	0.375	Voltage	4.1	Voltage	>=	4.1	003	StepTime	0:05:00	4NNN
3	Discharge	Current	0.375	Voltage	3.0	Voltage	<=	3.0	004	StepTime	0:05:00	4NNN
4	Loop 1					Loop Cnt	=	2	005			
5	Charge	Current	0.375	Voltage	4.1	Voltage	>=	4.1	006	StepTime	0:05:00	4NNN
6	AdvCycle											
7	Do 3											
8	Do 2											
9	Charge	Current	0.750	Voltage	4.1	Voltage	 	4.1	010	StepTime	0:05:00	4NNN
						StepTime	Ш	0:30:00	011	StepTime	0:05:00	
10	Rest					StepTime	=	0:30:00	011	StepTime	0:05:00	4YNN
11	Discharge	Current	1.500	Voltage	3.0	Voltage	<=	3.0	012	StepTime	0:05:00	4NNN
						StepTime	=	0:15:00	013	StepTime	0:05:00	
12	Rest					StepTime	II	0:15:00	013	StepTime	0:05:00	4YNN
13	AdvCycle											
14	Loop 2					Loop Cnt	=	199	015			
15	Charge	Current	0.375	Voltage	4.1	Voltage	 	4.1	016	StepTime	0:05:00	4NNN
16	Discharge	Current	0.375	Voltage	3.0	Voltage	۳	3.0	017	StepTime	0:05:00	4NNN
17	Charge	Current	0.375	Voltage	4.1	Voltage	 	4.1	018	StepTime	0:05:00	4NNN
18	AdvCycle									-		
19	Loop 3					Loop Cnt	II	1000	020	-		
20	End									-		

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